Journal of Magnetics 16(1), 23-26 (2011) DOI: 10.4283/JMAG.2011.16.1.023

Effects of Titanium Impurity on the Crystallographic and Spin-rotation Transitions of FeS

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(Received 8 October 2010, Received in final form 17 February 2011, Accepted 17 February 2011)

The effects of titanium ions on the crystallographic and spin-rotation transitions in iron sulfide have been examined by Mössbauer spectroscopy in the temperature range of 78 to 600 K. It is noted that the titanium impurity of $Ti_{0.02}Fe_{0.98}S$ affects both the crystallographic and spin-rotation transitions of the iron sulfide. 2% impurity of Ti^{2+} in FeS causes the increase in the difference between the spin rotation and α transition temperature by as much as 10 K compared with that for FeS. Both 1c and 2c structures coexist in the range between the α transition temperature and approximately 26 K, with a smaller hyperfine field corresponding to the 1c structure. The spin-rotation temperature for $Ti_{0.02}Fe_{0.98}S$ was measured to be 365 K, which is 10 K lower than the α transition temperature. By the 2% impurity of Ti^{2+} in FeS the Néel temperature appreciably is not affected.

Keywords : titanium, FeS, spin rotation, crystallographic transition

1. Introduction

Interesting crystallographic and magnetic phase transitions appear in iron sulfide FeS.

It was reported that the crystallographic α transition took place at approximately $T_\alpha \approx 400$ K in FeS [1]. According to the report, FeS exists in a NiAs structure above T_α and transforms to a hexagonal superstructure below this temperature. The length of the supercell c-axis is twice of the high-temperature phase. For that reason, the phases with the NiAs structure and the hexagonal superstructure will be called the 1c phase and 2c phase, respectively. Neutron-diffraction and magnetic susceptibility [2, 3] show that the FeS is antiferromagnetic with a Néel temperature of ~600 K. On comparison, for $Fe_{0.996}S$ the spin-rotation transition (the Morin transition T_M) takes place at a T_M temperature 31 K higher than T_α.

In this paper we present our Mössbauer measurements for $Ti_{0.02}Fe_{0.98}S$ in an effort to determine the effects of Ti ions on the crystallographic and magnetic transitions of iron sulfides. As the impurity ions $Ti^{2+}(3d^2)$ ions have smaller number of 3d electrons than that of $Fe^{2+}(3d^6)$ ions.

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2. Experimental

$Ti_{0.02}Fe_{0.98}S$ sample was prepared by direct reaction [4] of the elements. The starting materials were sulphur, iron, and titanium powders of 99.9999, 99.995, and 99.99% purity, respectively, accurately weighted by heating in an evacuated quartz tube. Mixtures of each elemental proportion sealed in vacuum quartz ampoules were first heated slowly to 600 ºC to prevent explosion due to sudden expansion of sulphur gas, and then they were kept at this temperature for one day, followed by further heating to 1000 ºC for seven days. After quenching down to room temperature in order to obtain a homogeneous material it was necessary to grind the sample and to press the powder into a pellet before the second annealing process at 1000 ºC in an evacuated and sealed quartz ampoule for three days. A third firing similar to the second one was required to obtain the single-phase sample.

Extra precaution has been taken during the sealing process to avoid sulfur vaporization as shown in Fig. 1 [5]. The quartz tube with two narrow necks was first filled with the desired amount of sulfur and then covered by one layer of titanium and iron powder each. These two layers block light from the torch and reduce thermal energy transfer from the torch to the sulfur. Additionally,

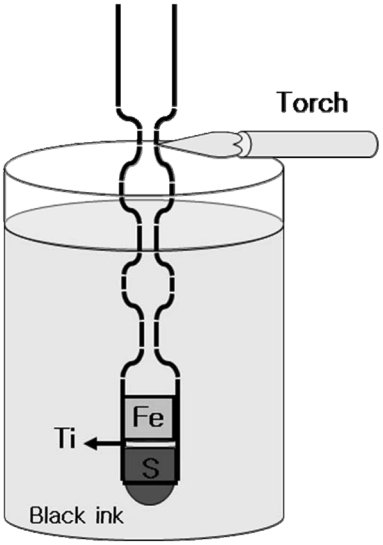

Fig. 1. Sealing Procedure.

the quartz tube was immersed into a liquid black ink bath to prevent sulfur vaporization due to the exposure to the light from the torch. Furthermore, the ink bath also can be used to cool the sample tube. During this sealing process the diffusion of sulfur vaporsinto the quartz tube is normally concerned. Since sulfur vapors in the sealed quartz ampoule would combine with iron and form solids on the tube wall during the initial heating at 450 ºC, at which temperature the diffusion is therefore negligible.

The sample was ^{57}Fe enriched to 5% of the metal atoms in the sample for Mössbauer measurements. Mössbauer spectra were recorded using a conventional electromechanical spectrometer manufactured by FAST Com Tec Ltd., which was set in a constant-acceleration mode with a 10 mCi ^{57}Co source in a rhodium matrix. To produce a uniform thickness over the detection area of the Mössbauer absorber, each sample was mixed with boron nitride powder and clamped between two thin boron nitride plates.

The measurements below room temperature were made in a cryostat with the thermal stability of 0.25 K while those above room temperature were obtained in a furnace with the stability being 0.30 K.

X-ray-diffraction patterns of $Ti_{0.02}Fe_{0.98}S$ at room temperature were obtained using a Rigaku diffractormeter with Cu $K\alpha$ radiation.

3. Results and Discussion

X-ray-diffraction patterns at room temperature showed that $Ti_{0.02}Fe_{0.98}S$ has the hexagonal superstructure. From which, the lattice parameters a_0 and c_0 were found to be

$a_0 = 0.9690 \pm 0.005$ Å and $c_0 = 11.6892 \pm 0.05$ Å.

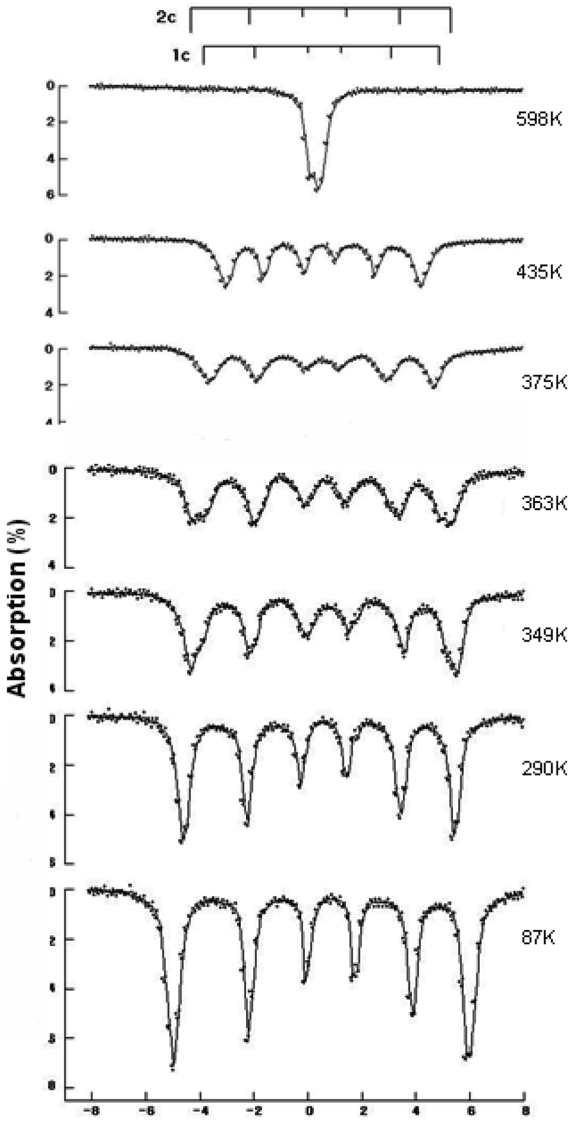

Fig. 2. Mössbauer spectra of $Ti_{0.02}Fe_{0.98}S$.

We have taken Mössbauer spectra of $Ti_{0.02}Fe_{0.98}S$ at various absorber temperatures ranging from 87 to 600 K. They are shown in Fig. 2, which illustrates the temperature variations in the Mössbauer spectra for $Ti_{0.02}Fe_{0.98}S$. There are 6 Mössbauer lines and all peaks are very intense at both the high and low temperatures while 12 lines are present for the intermediate temperatures, suggesting the coexistence of 1c and 2c phases [6].

Figs. 3 and 4 reveal the temperature dependence of the quadrupole splitting ΔE_Q and the magnetic hyperfine field H_{hf} for $Ti_{0.02}Fe_{0.98}S$, respectively. ΔE_Q was calculated from the positions of the Mössbauer absorption lines using the expression

$$\Delta E_Q = \frac{1}{4}(V_6 - V_5 + V_1 - V_2), \quad (1)$$

Where V_i represents the position of the ith absorption line in mm/s.

Using a least-squares computer program, one set or two of the six Lorentzian lines were fitted to the Mössbauer spectra below the Néel temperature under the following restraints [7], which are valid if the quadrupole interaction is much weaker than the magnetic hyperfine interaction:

$$E_1 = \delta + \Delta E_Q + \frac{1}{2}(3g_1 + g_0)\mu_N H,$$
$$E_2 = \delta - \Delta E_Q + \frac{1}{2}(g_1 + g_0)\mu_N H,$$
$$E_3 = \delta - \Delta E_Q + \frac{1}{2}(g_0 - g_1)\mu_N H, \quad (2)$$
$$E_4 = \delta - \Delta E_Q - \frac{1}{2}(g_0 - g_1)\mu_N H,$$
$$E_5 = \delta - \Delta E_Q - \frac{1}{2}(g_1 + g_0)\mu_N H,$$
$$E_6 = \delta + \Delta E_Q - \frac{1}{2}(3g_1 + g_0)\mu_N H,$$

where E_i stands for the line position of the ith absorption line in a six-line pattern. δ is the isomer shift. ΔE_Q represents the quadrupole shift:

$$\Delta E_Q = \frac{1}{8}e^2 qQ[e\cos^2\theta - 1 + \eta\sin^2\theta\cos(2\phi)], \quad (3)$$

where θ and ϕ are the angles, in polar coordinates, between the magnetic hyperfine field vector and the principal axes of the electric-field-gradient tensor. g_0 and g_1 represent the absolute values of g factors for the ground and the first excited levels of the ^{57}Fe nucleus, respectively. μN stands for the nuclear magneton and H is the magnetic hyperfine field [5]. Therefore, from Eq. (3) we expect that ΔE_Q would change considerably at the spin-rotation transition. It is apparent from Fig. 3 that Morin transition occurs at approximately 365 K which is 10 K lower than T_α, the α transition temperature marking the upper end of the coexistence region of the 1c and 2c phases as shown in Fig. 4. In Fig. 3 the quadrupole shift value for $Ti_{0.02}Fe_{0.98}S$ jumps abruptly at 365 ± 1 K corresponding to the spin rotation from lying in the [001] plane above the transition to the pointing along the [001] direction below, which was observed in FeS [2, 3]. In addition there seems to be some outliers near 375 K related to the α transition in Fig. 4. Furthermore, the coexistence region of the two phases for $Ti_{0.02}Fe_{0.98}S$ is much narrower than FeS [6] as can be seen in Fig. 4. It is found that 2% titanium impurity of the metal atoms in FeS lead to rapid crystallographic transition in a narrow temperature region of about 26 K, while the α transition in iron sulfide occurs over a wide temperature range of around 200 K. Moreover, the spin-rotation temperature is increased by 10 K below T_α while T_M for FeS is 24 K below T_α.

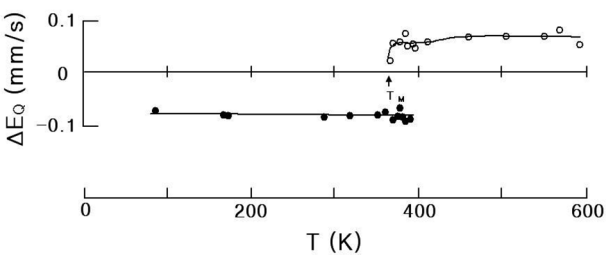

Fig. 3. Temperature dependence of the quadrupole splitting ΔE_Q for $Ti_{0.02}Fe_{0.98}S$.

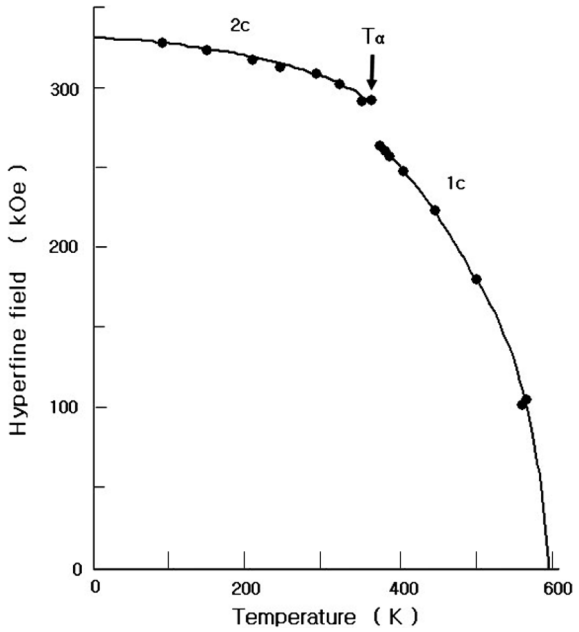

Fig. 4. Temperature dependence of the magnetic hyperfine field H_{hf} for $Ti_{0.02}Fe_{0.98}S$.

The Néel temperature of $Ti_{0.02}Fe_{0.98}S$ was determined to be 598 ± 2 K, implying that the 2% titanium impurity in FeS does not affect the superexchange interactions in the 1c phase appreciably.

4. Conclusion

In conclusion, $Ti^{2+}(3d^2)$ impurity speeds up the crystallographic transition in a narrow temperature region of 26 K whereas there is a wide temperature range of approximately 200 K in iron sulfide [6]. In contrast, $Ti^{2+}(3d^2)$ impurity decreases the spin-rotation temperature by 10 K below T_α while T_M for iron sulfide is 24 K below T_α.

Ackowledgements

This research was supported by the Yeungnam University research grants in 2008.

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