Fluorescence EXAFS study of residual Ga in $\beta$-FeSi$_2$ grown from Ga solvent

H Yamada$^1$, M Tabuchi$^2$, Y Takeda$^1$, and H Udono$^3$

$^1$ Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
$^2$ Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
$^3$ Department of Electrical and Electronic Engineering, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

E-mail: yamada-h@mercury.numse.nagoya-u.ac.jp

Abstract. Solution growth method is a suitable growth technique to obtain a large-sized and good crystalline quality $\beta$-FeSi$_2$ single crystal. However, during the solution growth method, solvent atoms are often automatically doped into the growing crystals and may affect properties of them. In this work, we investigated Ga atoms in $\beta$-FeSi$_2$ grown from a Ga solvent by EXAFS and discussed the effect of the Ga atoms on electrical properties of $\beta$-FeSi$_2$. The results of the EXAFS measurement indicated that 60% of Ga in $\beta$-FeSi$_2$ substituted Si sites, and 40% of them substituted Fe sites. The ab-initio calculation of electron density of states indicated that when the concentration of Ga in $\beta$-FeSi$_2$ is so high as 1.0 at%, the residual Ga is not the origin of the p-type conductivity of the $\beta$-FeSi$_2$ crystal grown from the Ga solvent. We should conduct further calculation to decide if the residual Ga is the origin of the p-type conductivity or not in the real $\beta$-FeSi$_2$ crystal with only 0.1 at% of Ga.

1. Introduction

$\beta$-FeSi$_2$ is one of the potential candidates for thermoelectric devices because of its high Seebeck coefficient, high working temperature, large working temperature range, high resistance to oxidation, and non-toxicity [1-3]. High quality single crystals of $\beta$-FeSi$_2$ are required for the thermoelectric devices. However, usual growth methods from a melt such as the Czochralski and Bridgman methods cannot be used for the growth of the $\beta$-FeSi$_2$ single crystals, since $\beta$-FeSi$_2$ is a stable phase at low temperature. Therefore much effort has been made on growing $\beta$-FeSi$_2$ single crystals with a good structural perfection by chemical vapor transport (CVT) method or solution growth method. However, crystals grown by the CVT method are needlelike and frequently twinned [4]. On the contrary, by the solution growth method, relatively large-sized and good crystalline quality $\beta$-FeSi$_2$ single crystals are obtained [5]. On the other hand, it has been shown that the conduction type of the $\beta$-FeSi$_2$ single crystals is always p-type when the $\beta$-FeSi$_2$ crystals are obtained by the solution growth method with Ga as the solvent [5]. It may be caused by the residual Ga in the crystal, although the details have not been understood yet.
In this study, we investigate the influence of the residual Ga atoms to the conduction type of the $\beta$-FeSi$_2$ crystals by extended X-ray absorption fine structure (EXAFS) analysis and ab-initio calculations of electron density of states.

2. Experiments
A sample was grown by temperature gradient solution (TGSG) method [6]. For the growth, a Ga-base Fe-Si solute (Fe:Si=1:2) were prepared as an arc-melted ingot. The purity of the source metals was 5N, 5Nup, and 6N for Fe, Si, and Ga, respectively. The solutes, Fe and Si, and the solvent, Ga, were charged in a purified quartz ampoule and the ampoule was sealed in a quartz rod. The growth region temperature, the source temperature and the temperature gradient were 880, 920ºC and 40ºC/cm, respectively, for the TGSG. After the solution growth, the sample was powdered and annealed at 950ºC for 10 hours to eliminate Ga inclusion.

The fluorescence-EXAFS measurement was conducted at beam line BL-12C at Photon Factory (PF) in High Energy Accelerator Research Organization. Ga-K fluorescence X-ray was detected using a 19-elements SSD while the incident X-ray intensity was detected by an ion chamber.

3. Results and discussion
The EXAFS analysis and ab-initio calculation on electron density of states were conducted to investigate the influence of the residual Ga to the conduction type of $\beta$-FeSi$_2$ crystal grown from the Ga solvent.

3.1. EXAFS analysis
Figure 1 shows measured EXAFS $k^3\chi(k)$ spectrum for the $\beta$-FeSi$_2$ sample grown from the Ga solvent. Figure 2 shows the Fourier transformed $k^3\chi(k)$ spectrum. The Fourier transformation was conducted in the $k$ range from 3.8 to 10.0 Å$^{-1}$. The peak observed at about 2.1 Å in figure 2 is corresponded to the first-nearest-neighbor shell. In order to investigate the first-nearest-neighbor shell, the spectrum was inverse Fourier transformed in the range from 1.65 to 3.20 Å and parameter fitting was conducted on the spectrum in $k$-space.

For the fitting, models in which Ga atoms were located at Si site, Fe site or interstitial site in $\beta$-FeSi$_2$ crystal were concerned. However, R-factor for the
fittings with these models was not low enough. Then a model in which Ga atoms were located at both Si site and Fe site in $\beta$-FeSi$_2$ crystal was concerned. Using the model, R-factor which was so low as 0.004 was obtained when the ratio of Ga on Si and Fe sites were about 60% and 40% respectively.

3.2. Ab-initio calculation of electron density of states

In order to discuss the influence of the residual Ga atoms in $\beta$-FeSi$_2$ to the conduction type, we calculated electron density of states using virtual crystal approximation (VCA) method [7]. For the calculation, a $\beta$-FeSi$_2$ model structure which consists of 32 Si atoms and 16 Fe atoms in a unit cell were constructed. In the calculation, we should consider a situation that Ga atoms replace both Si and Fe sites in the $\beta$-FeSi$_2$ crystal. However, when only one of the 32 atoms and only one of the 16 atoms are replaced by Ga atoms, the concentration of Ga in the $\beta$-FeSi$_2$ is up to about 4at%, although the real concentration of Ga in the sample is estimated to be 0.1at% from the fluorescence X-ray yield of Ga. The VCA method was adopted since we can calculate the electron density of states of a crystal with such a dilute impurities using the VCA method without taking large model structure. In the VCA method, same of the atoms in a model structure is treated to be a virtual atom of which property is mixture of two different atoms. Using the VCA method, we calculated the electron density of states of $\beta$-FeSi$_2$ with 1at% of Ga atoms (60% of them were on Si and 40% of them were on Fe sites). Figure 3 shows the result of the calculation. We also tried to calculate the electron density of states for a $\beta$-FeSi$_2$ crystal with 0.1at% Ga, however, the calculation did not converge. As shown in figure 3, some density of states appeared just above the valence band. Since the Fermi level was above the density of states which appeared in the band gap, the states should be filled by electrons and may not work as acceptors levels. In the other words, the calculation showed that the residual Ga in $\beta$-FeSi$_2$ was not the origin of the p-type conductivity of the $\beta$-FeSi$_2$. However the concentration of Ga was set at 1.0at% for the calculation, which was 10 times higher than in the real $\beta$-FeSi$_2$. Therefore, we should try the calculation for the $\beta$-FeSi$_2$ with 0.1at% of Ga using more powerful computer, in order to truly decide if the origin of the p-type conductivity is the residual Ga or not.

4. Conclusions

We investigate the influence of the residual Ga to the conduction type of $\beta$-FeSi$_2$ grown from the Ga solvent by EXAFS analysis and ab-initio calculation of electron density of states. EXAFS analysis indicated that about 60% of Ga located at Si site and about 40% of them located at Fe site in $\beta$-FeSi$_2$. The ab-initio calculation of electron density of state indicated that when the concentration of Ga in $\beta$-FeSi$_2$ is as high as 1.0at%, the residual Ga is not the origin of the p-type conductivity of the $\beta$-FeSi$_2$ crystal grown from the Ga solvent. We should conduct further calculation to decide if the residual Ga is the origin of the p-type conductivity or not in the real $\beta$-FeSi$_2$ crystal with only 0.1at% of Ga.

5. Acknowledgements

This work was performed as a part of the projects (Project No. 2007G558 and 2008G075) accepted by the Photon Factory Program Advisory Committee.
Reference

[1] Ito M, Nagai H, Katsuyama S and Majima K 2001 J. Alloys Compd., 315 251
[2] Ito M, Nagai H, Harimoto D, Katsuyama S and Majima K 2001 J. Alloys Compd. 322 226
[3] Chen Y H, Zhao B X, Lu F Y, Müller E and Mrotzek A 2003 J. Appl. Phys. 94 6621
[4] Wang F J, Saitou S, Ji Y S and Isshiki M 2006 J. Crystal Growth 295 129–132
[5] Udono H and Kikuma I 2004 Thin Solid Films 461 188–192
[6] Udono H and Kikuma I 2001 Jpn. J. Appl. Phys. 40 1367-1369
[7] Nordheim L 1931 Ann. Phys. 9 607