Anomalous behavior in $M$-$T$ curve of $\beta$-FeSi$_2$ single crystals

K Suga$^1$, E Ohmichi$^1$, T Osada$^1$, K Kindo$^1$, M Sasaki$^2$, A Ohnishi$^2$, M Saito$^2$, T Kikuchi$^2$, S Nonoyama$^3$ and S Adachi$^4$

$^1$ISSP, University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, 277-8581, Japan
$^2$Department of Physics, Faculty of Science, Yamagata University, Kojirakawa 1-4-12, Yamagata, 990-8560, Japan
$^3$Faculty of Education, Yamagata University, Kojirakawa 1-4-12, Yamagata, 990-8560, Japan
$^4$Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan

suga@issp.u-tokyo.ac.jp

Abstract. Zero-field-cooled (ZFC) and field-cooled (FC) magnetizations have been measured for $\beta$-FeSi$_2$ single crystals from 4 to 300 K up to 60 kOe using a SQUID magnetometer. The ZFC and FC magnetizations at low field below 500 Oe show the characteristic temperature dependence due to superparamagnetism (SP). The blocking temperature $T_B$ was well explained by the theory for the SP. We have found an anomalous peak (AP) at around 55 K, which is caused by some kind of magnetic transition. The AP is enhanced appreciably with increasing magnetic field but whose peak temperature is field-independent. Moreover, its magnetization develops temporally with the delay time 16.5 h.

1. Introduction

$\beta$-FeSi$_2$ has received considerable attention as an attractive material for optoelectronic and thermoelectric applications since it has many superior features such as sufficiently high figure-of-merit and absorption coefficient [1]. Therefore, the transport, thermoelectric and optical properties have been extensively studied. Especially, $\beta$-FeSi$_2$ shows a nonlinear Hall effect and a hysteresis effect in the Hall resistivity [2, 3]. These results were explained by anomalous Hall effect [2] or by the contribution of two types of carriers [3]. So far, the articles to support the latter are few. For the former, the long-time relaxation of remanent Hall voltage, observed for the Cr-doped $\beta$-FeSi$_2$, was explained by the superparamagnetic clusters [2].

In this study, we investigated the magnetic properties of $\beta$-FeSi$_2$ single crystals in the temperature range of 4 – 300 K using a SQUID magnetometer up to 60 kOe. We found that the Zero-field-cooled (ZFC) and field-cooled (FC) magnetizations at low field below 500 Oe show the characteristic temperature dependence due to superparamagnetism (SP), which is due to the aggregates of the excess
Fe atoms. The blocking temperature was well explained by the theory for the SP. We also found that a narrow anomalous peak (AP) appears at around 55 K, which is caused by some kind of magnetic transition. The AP shows quite unusual behaviors that its magnetization develops temporally with a long delay time.

2. Experiment

The single crystals of β-FeSi$_2$ were grown by chemical vapor transport technique using I$_2$ as a transport agent. The grown crystals have needle-like shape with length of about 4 mm along [010] axis and diameter of about 1 mm. The mass of sample was about 0.5 mg. The crystal structure was examined by the X-ray diffraction to agree with the reported data.

Magnetization data were taken for one single crystal in the temperature range of 4 – 300 K up to 60 kOe using a SQUID magnetometer. Sample was held on glass board by fluoroplastic heat shrinkable tube and then set in polyethylene straw. The magnetic field was applied perpendicular to [010] axis. The $M$-$T$ experiments under the ZFC and FC conditions were done during increasing temperature, the $M$-$B$ experiments were done during increasing field, and for the long time magnetization experiments the sample was cooled down from room temperature to 55 K in zero field and then the data were taken at 60 kOe.

3. Results and discussions

Figure 1 shows the temperature dependences of the ZFC and FC magnetization $M$ observed at low field of (a) 100 - 500 Oe and at high field of (b) 5 and 60 kOe. In the low field range below 500 Oe, both ZFC and FC magnetizations increases slightly with decreasing temperature and show small peak at around 55 K. Then, below the blocking (or spin glass) temperature marked by the arrows, the ZFC and FC curves become to separate each other, i.e., the ZFC curve deviates downward from the FC curve. Such behavior can be seen commonly in a SP or a spin glass (SG). According to the theoretical analysis of the characteristic temperature described shortly later, however, the magnetism of the present system should be not due to the SG but due to the SP. The blocking temperature $T_b$ decreased appreciably with increasing magnetic field and then above 5 kOe we did not obtain the value of $T_b$ because whose value should be less than our lowest temperature. As predicted theoretically for the SP [4], the reduced blocking temperature $t_b$ (= $1 - T_b(B)/T_b(0)$; $T_b(0)$ and $T_b(B)$ denote the values of $T_b$ at $B = 0$ and $B$, respectively) can be expressed by the form: $t_b = A h^{2/3}$ ($h$ = $\mu B/2E_0$; $E_0$ denotes the anisotropy energy). The values of $t_b$ were calculated using $T_b(0)$ = 90 K, and then we obtained a good linearity of $t_b$ against $B$ with the slope of 2/3, as shown in Fig. 2. This result gives us a strong evidence for the SP.

![Figure 1](image1.png)  
Figure 1. ZFC and FC magnetization curves observed at low field of (a) 100 - 500 Oe and at high field of (b) 5 and 60 kOe: the open and closed symbols denote the FC and ZFC magnetization curves. The arrows mark the blocking temperature $T_b$. 

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From Fig. 2, one can see that $t_b$ is larger than the unity for $B$ larger than 5 kOe. This suggests that the blocking temperature disappears above 5 kOe. Hence, we could not observe the characteristic SP behavior in Fig. 1(b). From Fig. 1(b), furthermore, we found the Curie-Weiss like magnetization at low temperature and the enhancement of the AP around 55 K ($\equiv T_p$). The former may be attributed to the paramagnetism (PM) due to the magnetic impurity as observed for many materials including magnetic impurities. This fact suggests that in the present system there co-exist the ferromagnetic aggregates of excess Fe atoms contributing the SP and isolated Fe atoms contributing the PM. Furthermore, we focused on the AP observable only around $T_p$.

To clarify the AP, we have performed the magnetization experiments at various temperatures (especially at around $T_p$). The magnetization curves at (a) 40 K below $T_p$, (b) 50 K near $T_p$ and (c) 70 K above $T_p$ are shown in Fig. 3. In the experiments, each magnetization measurement was repeated three times. The magnetization curves below and above $T_p$ are temporal-independent, while the curve
near $T_p$ is enhanced step by step with repeated runs (each run takes about 1 hour). This suggests that the magnetization near $T_p$ exhibits a long-time magnetization: one example observed at 55 K and 60 kOe is shown in Fig. 4. To our knowledge, such long-time magnetization has never been reported yet. The linear components in the $M$-$B$ curves except for that at 50 K may be due to the isolated Fe atoms as magnetic impurities or the paramagnetic $\beta$-FeSi$_2$ itself. We found that the temporal magnetization $M(t)$ can fit the delayed form $M(t) = M_0 + C[1- \exp(-t/\tau)]$ ($M_0$: the spontaneous magnetization at time $t = 0$; $C$: the constant; and $\tau$: the delay time). The value of the delay time was obtained to be $\tau = 16.5$ h from the best-fit curve (the white line in Fig. 4).

As can be seen from Fig. 1(b), when the temperature is increased from 4 K the magnetization changed abruptly at around 48 K just like a magnetic transition from the SP to some other magnetic phase, though its sharpness becomes blurry with decreasing magnetic field. However, though not shown here, no transition appears when the temperature is decreased rapidly from 300 K. It suggests that the phase transition involves extremely wide hysteresis. To understand the fundamental nature of the AP, it is necessary to perform further detailed experiments.

4. Summary
Magnetization has been measured for $\beta$-FeSi$_2$ single crystals from 4 to 300 K up to 60 kOe using a SQUID magnetometer. Temperature dependences of magnetization measured under FC- and ZFC-conditions show a superparamagnetic behavior with a blocking temperature $T_b = 20$ K at 500 Oe. The AP in $M$-$T$ curve was found for both FC- and ZFC-processes at around 55 K. The AP became clear with increasing magnetic field, while whose position is field-independent. Moreover, in the temperature range where the AP appears, the slope of $M$-$B$ curve increases with applying magnetic field repeatedly.

References
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Figure 4. Long-time magnetization at 55 K for 60 kOe.