Search for spontaneous magnetization in noncentrosymmetric superconductors

A Sumiyama1, D Kawakatsu1, J Gouchi1, I Kawasaki1, A Yamaguchi1, G Motoyama2, Y Hirose3, R Settai3 and Y Onuki4

1 Graduate School of Material Science, University of Hyogo, Kamigori, Hyogo 678-1297, Japan
2 Department of Material Science, Shimane University, Matsue, Shimane 690-8504, Japan
3 Department of Physics, Niigata University, Nishi-ku, Niigata 950-2181, Japan
4 Department of Physics and Earth Sciences, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan

E-mail: sumiyama@sci.u-hyogo.ac.jp

Abstract. We have measured the magnetization of two noncentrosymmetric superconductors: Ir2Ga9 and CePt3Si using a SQUID magnetometer, neither of which has been tested for the time-reversal symmetry in the superconducting state. For Ir2Ga9, the magnetization change $\Delta M$ below the superconducting transition temperature $T_c \approx 2.2$ K was smaller than $10^{-5}$ G in zero magnetic field, suggesting that $\Delta M$ originates in the Meissner effect induced by the possible residual field. When CePt3Si was cooled in zero magnetic field, $\Delta M$ along the $c$ axis first decreased below $T_{c0.75}^+$ and then increased below $T_{c0.45}$ (bulk superconducting phase). Since this behavior cannot be explained by the Meissner effect, it may be a sign of a spontaneous magnetization.

1. Introduction

Since the discovery of noncentrosymmetric superconductor CePt3Si[1], various kind of superconductors, of which crystal structures lack a center of inversion symmetry, have been investigated, because such structure allows the coexistence of spin-singlet and spin-triplet states and may induce superconductivity other than the conventional BCS (s-wave, spin-singlet pairing) state. Recently, LaNiC2 has been reported to be in the broken time-reversal symmetry (BTRS) state, based on the observation of a spontaneous magnetic field below the superconducting transition temperature $T_c$ by $\mu$SR measurements[2], although NQR measurements indicated conventional BCS-type superconductivity[3]. Very recently, we have investigated the magnetization of LaNiC2 and found that a spontaneous magnetization in the $c$-axis direction appears below $T_c$ and is closely related to the crystal structure lacking inversion symmetry along the $c$ axis[4]. It will be interesting to investigate other noncentrosymmetric superconductors and clarify whether a spontaneous magnetization in the superconducting state is a common property or peculiar to LaNiC2. In this paper, we have investigated two noncentrosymmetric superconductors Ir2Ga9 and CePt3Si, a spontaneous magnetic field of which has not been verified in the superconducting state by $\mu$SR measurements thus far.

The noncentrosymmetric superconductor Ir2Ga9 has the monoclinic (distorted Co2Al-type) structure with the space group $Pc$. It was reported to be a type-II BCS superconductor first[5], and then classified as type-I through the study of a single crystal[6]. The de Haas-van Alphen
experiments have revealed that splitting energies between the two Fermi surfaces caused by the antisymmetric spin-orbit interaction are 290 and 130K for $\alpha$ and $\beta$ branches, respectively[7]. No experimental results that suggest unconventional superconductivity have been reported yet.

The heavy-fermion superconductor CePt$_3$Si has the crystal structure (tetragonal, space group $P4mm$) and lacks the inversion symmetry along the $c$ axis. A large number of studies have been done on its unconventional superconductivity[8], and yet the spontaneous magnetic field in the superconducting state remains unknown; a large internal field (~160 G) by the coexisting antiferromagnetism has been observed below $T_N \sim 2.2$ K by $\mu$SR measurements, while a slight change of the internal field below $T_c$, which is at the limit of the measurement accuracy, is ascribed to a coupling of the superconducting and magnetic order parameters and/or to the decrease of the hyperfine contact contribution acting on the muon[9].

2. Experimental

A single crystal of Ir$_2$Ga$_9$ was grown by the Ga-self flux method. The details of the growth conditions were given in the previous paper[7]. The critical temperature determined in dc resistivity measurements was 2.2 K. A piece of sample with flat (001) and (100) planes and about the size of 2 mm was made out of the ingot.

A single crystal of CePt$_3$Si, which has the tetragonal structure (space group $P4mm$) was grown by the Bridgman method. The details of the sample preparation were given in previous papers[10, 11]. A piece of crystal was cut from the ingot into a cubic shape with edges of about 3 mm along the [100] ($a$-axis), [010] and [001] ($c$-axis) directions. It was already used for the measurements of magnetic susceptibility[12] and the Josephson effect[13]. Although it shows a single peak at 0.4 K in the temperature dependence of specific heat[12], the Meissner effect appears below 0.75 K, suggesting the inclusion of a trace of high-$T_c$ phase ($T_c^{+} \sim 0.75$ K) besides the bulk superconducting phase ($T_c^{-} \sim 0.45$ K).

The magnetization was measured using a SQUID magnetometer linked to an astatic pair of pick-up coils. The sample and a reference superconductor In was inside one of the pick-up coils, and another reference Ta was inside the other. To eliminate the Meissner effect by the residual field, the earth’s magnetic field was reduced by a double-layered $\mu$-metal shield and a Cryoperm 10$^\circ$ shield outside the vacuum can. Outside the pick-up coils, a solenoid coil was wound to apply a small magnetic field. The residual field at In or Ta position was determined with an accuracy of 50 $\mu$G by applying a magnetic field to compensate the Meissner effect induced by the residual field. The details of the measurements are described in our previous paper[14].

3. Results and discussion

Figure 1 shows the temperature dependence of dc magnetic susceptibility around the superconducting transition. The sample was first cooled below $T_c$ in zero field and then $H_{dc}=15$ mOe was applied. The change in susceptibility indicates the diamagnetism caused by a shielding current. The sample was then warmed to temperatures above $T_c$ and the diamagnetic susceptibility (zero-field cooled susceptibility: $\chi_{ZFC}$) was measured. In the same field, the sample was cooled again to measure field cooled susceptibility ($\chi_{FC}$), which indicates the Meissner effect. Both samples show full diamagnetism $4\pi\chi_{ZFC} = -1$, which is confirmed in comparison with the full diamagnetism of In.

For Ir$_2$Ga$_9$, a sharp transition is observed at 2.2 K, and $\chi_{ZFC}$ deviates from zero at a higher temperature $\sim 2.7$ K. For CePt$_3$Si, notwithstanding that the sample showed a single peak at 0.4 K in specific heat measurements, both $\chi_{ZFC}$ and $\chi_{FC}$ show transition below 0.75K, suggesting that a high-$T_c$ phase ($T_c^{+} \sim 0.75$ K) is still contained. The Meissner fraction $\chi_{FC}/\chi_{ZFC}$ is 0.37 for Ir$_2$Ga$_9$ ($H \parallel c$) and 0.12, 0.06 and 0.1 for CePt$_3$Si ($H \parallel c$, $H \parallel a_1$ and $H \parallel a_2$), respectively, where $a_1$ and $a_2$ indicate two $a$-axis directions of the rectangular parallelepiped sample. The larger Meissner fraction as well as the narrower transition width suggests that the quality of Ir$_2$Ga$_9$
Figure 1. Temperature dependence of magnetic susceptibility $\chi$ for (a) $\text{Ir}_2\text{Ga}_9$ and (b) $\text{CePt}_3\text{Si}$, as obtained by the field-cooled and the zero-field cooled methods. The applied field is 15 mOe.

crystal is better than that of $\text{CePt}_3\text{Si}$; lattice defects and/or impurities that act as pinning sites are less included in $\text{Ir}_2\text{Ga}_9$.

The temperature dependences of magnetization change $\Delta M = M(T) - M(3\text{K})$ for $\text{Ir}_2\text{Ga}_9$ and $\Delta M = M(T) - M(1\text{K})$ for $\text{CePt}_3\text{Si}$ were measured in the cooling process in various magnetic fields, as shown in Fig. 2. The magnetization was calculated on the assumption that the magnetization change due to the full diamagnetism in Fig. 1 corresponds to $-1/4\pi \times 15$ mOe neglecting the demagnetizing effect. For $\text{Ir}_2\text{Ga}_9$, a sharp transition is observed within the range of applied fields (< 75 mOe). The magnetization change of $\text{CePt}_3\text{Si}$, on the other hand, clearly shows a superconducting transition below $T_c^+ \sim 0.75$ K even in the largest field. This result suggests that the relatively large magnetization change in the high-$T_c$ phase in spite of its small amount, which is below the limit of detection in specific heat measurements, cannot be explained by some mechanism that is susceptible to magnetic field, such as Josephson network between the high-$T_c$ inclusions.

A test of a spontaneous magnetization in $\text{Ir}_2\text{Ga}_9$ is shown in Fig. 3. As shown in the inset, the residual field was different between Ta and In positions. Hereafter, we use the residual field at the In position as the residual field $H_{\text{res}}$ at the sample position, and regard $H = H_a + H_{\text{res}}$ instead of the applied field $H_a$ as the magnetic field at the sample position. The magnetization

Figure 2. Temperature dependence of magnetization change $\Delta M$ in various magnetic fields, where (a) $\Delta M = M(T) - M(3\text{K})$ for $\text{Ir}_2\text{Ga}_9$ and (b) $\Delta M = M(T) - M(1\text{K})$ for $\text{CePt}_3\text{Si}$. 
change $\Delta M = M(T) - M(3\text{K})$ in $H = 0$ increases slightly at $T_c \sim 2.2$ K. However, this increase can be compensated by applying $H = 0.05$ mOe, which is much smaller than the typical residual field. Even if we compensate the residual field using the value at the In position, the residual field inevitably exists at the sample position by its spatial variation. Thus, the observed magnetization change can be explained by the Meissner effect induced by the possible residual field and cannot be regarded as a spontaneous magnetization within our experimental accuracy.

As shown in Fig. 3(b), the change in $\Delta M$ in $H = 0$ was reproduced in three cooling processes (1, 3, 4) and also in the warming process (2). This behavior indicates that the motion of the magnetic flux is reversible in Ir$_2$Ga$_9$ and contrasts with that of LaNiC$_9$, in which an abrupt fluctuation appeared at $T_c$ in the warming process[4].

Figure 4 shows the magnetization change $\Delta M = M(T) - M(1\text{K})$ along the $c$ axis of CePt$_3$Si. Because of the inclusion of the high-$T_c$ phase ($T_c^+ \sim 0.75$ K), $\Delta M$ begins to change below 0.75 K and shows a complicated behavior; in zero magnetic field, $\Delta M$ first decreases below 0.75 K and then begins to increase below the bulk $T_c^- \sim 0.45$ K. This behavior is reproducible both in the cooling and warming processes, as shown in Fig. 4(b). When a small magnetic field is applied, $\Delta M$ at each temperature increases or decreases according to the direction of the applied magnetic field regardless of whether the temperature is above or below $T_c^-$. Even in $H = 0.75$ mOe, the abrupt upturn at $T_c^-$ is still observed. These results indicate that the Meissner effect induced by the applied field points in the same direction in the two superconducting phases, and therefore the opposite evolution of $\Delta M$ in zero magnetic field cannot be explained by the Meissner effect induced by the possible residual field.

The magnetization change $\Delta M = M(T) - M(1\text{K})$ along the $a$ axis is also complicated, as shown in Fig. 5. Although the two $a$-axis directions of CePt$_3$Si should be crystallographically equivalent, the present crystal shows a difference in field-cooled susceptibility between the two $a$-axis directions, which are denoted as $a_1$ and $a_2$ axes, as shown in Fig. 1. In zero magnetic field, $\Delta M$ along the $a_2$ axis changes little below either $T_c^+$ or $T_c^-$, suggesting the absence of a spontaneous magnetization. In contrast, $\Delta M$ along the $a_1$ axis increases rapidly below $T_c^+$ and decreases slowly below $T_c^-$ in $H = 0$. By applying magnetic fields, the Meissner effect is induced below $T_c^+$ in the $a_2$-axis direction, while in the $a_1$-axis direction the Meissner effect between $T_c^-$ and $T_c^+$ is small as compared with the increase in $\Delta M$ appeared in zero magnetic field; even in $H = 0.75$ mOe, where the change in $\Delta M$ below 1 K is compensated at 0.2 K, the increase in

![Figure 3](image)

Figure 3. Temperature dependence of magnetization change $\Delta M = M(T) - M(3\text{K})$ of Ir$_2$Ga$_9$ in (a) small magnetic fields and (b) zero magnetic field, where the data in (b) were measured in the cooling process (1,3,4) or the warming process (2). The data are shifted vertically by 0.01 mG for clarity. The inset in (a) indicates the residual field at the position of the standard superconductors (In, Ta).
\[ \Delta M = M(T) - M(1K) \]

Figure 4. Temperature dependence of magnetization change \( \Delta M = M(T) - M(1K) \) along the \( c \) axis of CePt\(_3\)Si in (a) small magnetic fields and (b) zero magnetic field, where the data in (b) were measured in the cooling process (1,3) or the warming process (2). The data are shifted vertically by 0.005 mG for clarity. The inset in (a) indicates the residual field at the position of the standard superconductors (In, Ta).

\( \Delta M \) below \( T_c^+ \) is still seen.

Since this crystal shows a single peak at 0.4 K in specific heat measurements, it should contain only a small amount of high-\( T_c \) (\( T_c^+ \)) phase. If we focus on the bulk \( T_c^- \) phase in \( H = 0 \), \( \Delta M \) changes a little (\(< 0.002 \, \text{mG}\)) below \( T_c^- \) in both \( a_1 \)- and \( a_2 \)-axis directions, while the increase in \( \Delta M \) along the \( c \) axis is larger (\( \sim 0.05 \, \text{mG}\)). This result may suggest that a spontaneous magnetization of the bulk \( T_c^- \) phase appears along the \( c \) axis. The high-\( T_c \) phase, on the other hand, also shows a change in \( \Delta M \) below \( T_c^+ \), which may also be ascribed to a spontaneous magnetization.

Although it is still unclear how the high-\( T_c \) phase exists in the sample, the result that the magnetization changes remarkably above \( T_c^- \) in spite of its small amount may suggest that the demagnetizing factor of the shape of the high-\( T_c \) inclusions enlarges the apparent change in \( \Delta M \). Then the anisotropy observed above \( T_c^- \) depends on the state of the shape.

Figure 5. Temperature dependence of magnetization change \( \Delta M = M(T) - M(1K) \) along the two \( a \) axes of CePt\(_3\)Si: (a) the \( a_1 \) axis and (b) \( a_2 \) axis, which correspond to those in Fig. 1. The insets indicate the residual field at the position of the standard superconductors (In, Ta) for each measurement.
and the configuration of the high-$T_c$ inclusions rather than the crystallographic directions. One possible explanation for the origin of such high-$T_c$ inclusions has been proposed in our previous papers\[15, 16\]: extended atomic bonds around crystallographic defects, dislocations, and stacking faults induce a lower pressure than the surroundings and lift the local $T_c$. This explanation also allows the appearance of a spontaneous magnetization below $T_c^+$, if the bulk $T_c^-$ phase shows a spontaneous magnetization below $T_c^-$. This explanation, however, contradicts the NMR measurements; the bulk $T_c^-$ phase and the high-$T_c$ phase indicate unconventional and conventional BCS superconductivity, respectively\[17\]. To ensure the spontaneous magnetization of CePt$_3$Si, further work on single crystals of different quality is in progress.

4. Conclusion
We have measured the temperature dependence of magnetization of Ir$_2$Ga$_9$ and CePt$_3$Si, and found no spontaneous magnetization within the experimental accuracy for Ir$_2$Ga$_9$. The magnetization change caused by the high-$T_c$ inclusions and the bulk superconducting phase of CePt$_3$Si, on the other hand, cannot be explained by the Meissner effect induced by the residual field and suggests the appearance of a spontaneous magnetization.

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