Anomalous phase of magnetic quantum oscillations by broken time-reversal symmetry

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\textbf{ABSTRACT}

The behavior of conduction electrons on magnetic structures has been intensely investigated. A typical example is the anomalous Hall effect in a ferromagnet. However, distinguishing various anomalous and normal Hall signals induced from the time-reversal symmetry (TRS) broken by their magnetic structure or applied magnetic field is delicate. In this study, we present a method to investigate TRS broken by the magnetic structure by analyzing magnetic quantum oscillations (MQOs). As is known, if a material is nonmagnetic, the MQO phases can only be two distinct values of 0 or $\pi$ from the orbits. When the magnetic structure breaks the TRS, the MQO phase deviates from these values, and the deviation is called the anomalous phase. We observed the anomalous phase in Fe-doped NbSb\textsubscript{2}, where magnetic Fe impurities break the TRS. The phase of a high-doped sample largely deviates from the phases of low-doped and pristine samples, indicating the anomalous phase. In MQOs, different types of magnetic structures afford different field dependence to the phase; this makes it easy to discern different magnetic structures, which respond differently with magnetic fields. This method can complement the Hall measurement and will provide useful information by itself for studying the magnetic structure of materials.
The performance of conduction electrons on magnetic structures has been intensively studied for both academic purposes to verify the interaction mechanism between them and potential application as spintronics devices [1–9]. In general, the behavior of conduction electrons in magnetic materials is distinct from that in nonmagnetic materials because of their broken time-reversal symmetry (TRS). Hall measurement is one of the most popular measurement methods employed to study such behavior of conduction electrons with broken TRS since the antisymmetric components of the conductivity tensor are only possible with the broken TRS via the Onsager reciprocal relation [10,11]. The effect of broken TRS by magnetic fields and magnetization are manifested in normal and anomalous Hall effects, respectively [2]. Recently, the studies on the Hall effects have been extended to the topological Hall effect from the noncollinear spin structure [4,12,13] and the nonlinear Hall effect from the current-induced magnetization [14–17]. However, Hall measurements gauge the total effect of broken TRS, which makes separating tiny signals generated by a particular source from the predominant signals generated by other sources difficult. For example, when we measure the Hall effects of a paramagnetic sample, separating the effect of magnetization from that of magnetic fields is difficult.

Magnetic quantum oscillations (MQOs) are regarded as a tool for probing the Fermi surface of a material and are used to study the Fermi-surface area, the cyclotron mass, the relaxation time, and the Berry phase [18–21]. However, the possibility of investigating the Fermi-surface symmetries using MQOs has been only recently broached. In a recent study, the phase constraint rules for MQOs classified by ten symmetry classes were theoretically verified [22]. The constraint rules can be experimentally checked by examining whether the phase constraint rules are satisfied with the Fermi-surface symmetries. In this study, we focus on TRS. With TRS, the MQO phases can only be two distinct values of 0 or π from the orbits. Thus, if other values are observed in the MQO phases (i.e., the anomalous phase), the system denotes broken TRS. The virtue of the anomalous phase is that it effectively manifests the zero-field magnetic response of the system [23], indicating that no subtlety arises from the effect of TRS broken by magnetic fields.

Herein, we experimentally show the existence of the anomalous phase in a magnetic-doped semimetal NbSb₂. NbSb₂ is a nonmagnetic and centrosymmetric semimetal with spin-degenerate orbits [21,24,25]. In our previous study on NbSb₂, when we tried to control the MQO phases by changing the direction of the applied magnetic field, two distinct values of the phase were observed [21]. This implies that TRS was preserved in NbSb₂ with zero magnetic field. Herein, we introduce Fe impurities to NbSb₂ and break the TRS using magnetic Fe impurities. We observe that anomalous phases develop with increasing Fe doping ratio.
magnetic impurities was explained using the exchange field and spin-dependent scattering [18,26]. In this study, we suggest an alternative explanation incorporating spin-orbit coupling (SOC) and the tilting of spins, which is intuitively applicable to a system’s magnetic structure.

Experimental data of pristine NbSb$_2$ and four Fe-doped NbSb$_2$ with different doping ratios are shown (see Supplementary Section 1, Fig. S1 for the synthesis method and sample characterization). The four Fe-doped samples are labeled as Fe1–Fe4, where the higher number denotes a higher Fe doping ratio. In all the study data, we apply the magnetic field along the crystal b-axis, which is the elongated direction of crystals. Fig. 1 shows the temperature-dependent susceptibilities from pristine NbSb$_2$ to Fe4. Pristine NbSb$_2$ and Fe1 manifest a temperature-independent diamagnetic signal. In fact, the magnetization of Fe1 is almost the same as that of pristine NbSb$_2$ because of its very small doping ratio. For Fe2–Fe4, we observe paramagnetic signals, which increase with the Fe doping ratio. The temperature-dependent susceptibility curves of Fe3 and Fe4 are fit with the Curie–Weiss law (see the inset of Fig. 1). For pristine NbSb$_2$, Fe1, and Fe2, the fitting could not be performed as their paramagnetic signals are weak. We estimated the Fe doping ratios from the fitting by assuming that the valency of Fe is Fe$^{3+}$, yielding doping ratios of 0.18% and 0.52% for Fe3 and Fe4, respectively. The background susceptibilities from the fitting are $\chi_0 \sim -6.4 \times 10^{-5}$ and $0.1 \times 10^{-5}$ emu/molOe for Fe3 and Fe4, respectively. We also observed the paramagnetic signals in the magnetic field-dependent magnetization (see Fig. S2 in Supplementary Materials).

Now, we focus on the Fe effect on MQOs. The oscillations of magnetization in a three-dimensional spin-degenerate system can be expressed by the sum of oscillations from spin up and down orbits as $-\sin(2\pi F/B - \pi + \lambda_{up} + \delta) - \sin(2\pi F/B - \pi + \lambda_{down} + \delta) = -2\cos\lambda_{as}\sin(2\pi F/B - \pi + \lambda_{s} + \delta)$, where $F$ is the frequency of oscillation, $\lambda_{as}$ is the phase of spin up (down) orbits, $\lambda_{as} = (\lambda_{up} + \lambda_{down})/2$ and $\lambda_{s} = (\lambda_{up} - \lambda_{down})/2$ are the asymmetric and symmetric phase, respectively, and $\delta$ is the phase from the curvature of three-dimensional Fermi surfaces [21,22]. Incorporating the high-order harmonics and the reduction factor from the finite temperature, relaxation time, and the dimensionality of the system, the oscillations of magnetization are as follows [18,20–22]:

$$\Delta M(p) = -M_0\sqrt{B}R_e(p)R_0(p)\cos p\lambda_{as}\sin[p\frac{2\pi F}{B} - \pi + \frac{\pi}{2}(1 - \text{sign}(p\lambda_{as})) + p\lambda_{s} + \delta],$$

where $p$ is the order of harmonics and $M_0$ is the dimensional constant. In addition, $R_T = (p\alpha T\beta)\sinh(p\alpha T\beta)$ and $R_D = \exp(-p\alpha T\beta/B)$ are the temperature-reduction and Dingle-reduction factors, respectively, where $\alpha$ =
$2\pi^2 e^2 m_s k_B / \hbar$ and $T_D = \hbar / 2\pi k_B \tau$ is the Dingle temperature. Here, $\lambda_{ae}$ is the phase difference between the oscillations from spin up and down orbits, and it affects the amplitude of total oscillation. On the other hand, $\lambda_{ape(dow)n}$ comprises the Berry curvature as well as orbital and spin magnetizations, which are time-reversal odd quantities. Therefore, $\lambda_a = 0$ with TRS. In contrast, if the TRS is broken by the magnetic structure, nonzero $\lambda_a$ can be obtained. The nonzero $\lambda_a$ is called the anomalous phase. Eq. (1) is useful for materials with almost spin-degenerate orbits, whose TRS is perturbatively broken. Since pristine NbSb$_2$ has a nonmagnetic centrosymmetric crystal structure, it has spin-degenerate orbits. Thus, the Fe impurities perturbatively can break the TRS via the paramagnetic impurities in the Fe-doped samples because of the tiny doping ratios.

First, we discuss the harmonics method and discuss how $\lambda_{ae}$ changes with the Fe impurities. First, we discuss the harmonics method. The relation

$$\frac{\cos 2 \lambda_a}{\cos \lambda_a} = \sqrt{2} \frac{A_b(2) R_g(1) R_e(1)}{A_b(1) R_g(2) R_e(2)}$$

can be obtained by dividing the amplitude part of the second harmonics with that of fundamental harmonics in Fig. 2(a) shows the magnetizations for pristine NbSb$_2$, Fe1, Fe2, and Fe3 in a strong field range (5.5~7 T). The MQO of Fe4 is unobservable. The amplitude of MQOs decreases with increasing Fe doping ratio, which subsequently decreases the relaxation time. For Fe3, MQOs were barely identified [see the inset of Fig. 2(a)]. We subtract the smooth nonoscillatory background from the magnetization data and conduct Fast Fourier transform (FFT) for a field range of 5~7 T. Fig. 2(b) shows the frequency-dependent FFT amplitudes. We then define $\xi$, $\alpha$, $\beta$, and $2\beta$ (the second harmonics of $\beta$) oscillations. For Fe3, only $\beta$ is observable. Here, we analyze the most predominant $\beta$ oscillations. Observed frequencies of $\beta$ oscillations from the FFT peaks are 700 T for pristine NbSb$_2$, Fe1, Fe2, and Fe3. We estimate the cyclotron masses using the temperature-dependent FFT amplitudes of $\beta$ oscillations (see Supplementary Section 2 and Fig. S3). The estimated cyclotron mass is $0.51 m_e$ for pristine NbSb$_2$, Fe1, Fe2, and Fe3. Since the frequencies of oscillations and the cyclotron masses are the same from pristine NbSb$_2$ to Fe3, we conclude that Fe impurities only afford perturbative effects on the band structures. We also estimate the relaxation times $\tau$ from the field-dependent amplitudes of $\beta$ oscillations (see Supplementary Section 2 and Fig. S3). The estimated relaxation times are 8.28, 3.61, and 1.05 ps for pristine NbSb$_2$, Fe1, and Fe2, respectively. In Fe3, they are unresolvable. As expected, the relaxation times decrease with increasing Fe doping ratio. This implies that the scattering between the conduction electrons and Fe impurities is significant, although the Fe impurities have a small effect on the overall band structure. The large sensitivity to the impurities denotes that the crystal quality of the pristine sample is excellent.

Here, we estimate $\lambda_{ae}$ with two methods (the harmonics and intercept methods) and discuss how $\lambda_{ae}$ changes with increasing Fe doping. The relation
Eq. (1); thus, we can evaluate $|\cos 2\lambda_u|/|\cos \lambda_u|$ from the measured amplitude ratio $A(2)/A(1)$. Subsequently, we can evaluate $|\cos \lambda_u|$ and four experimentally distinct values of $\lambda_u$ in a $[0, 2\pi)$ range. Since we verified that $\lambda_u$ is in the $[0.5\pi, \pi)$ range when the field is along the crystal b-axis in our previous study, we select this range herein. The estimated $\lambda_u$ are 0.622$\pi$, 0.617$\pi$, and 0.589$\pi$, which decrease with increasing Fe doping ratio. Since $\lambda_{up(down)}$ is related to the Zeeman coupling of the magnetic moment at the Fermi surface, decreasing $\lambda_u$ values denote that the z-component (the field direction) of the magnetic moments at the Fermi surface is reduced by the Fe impurities. This reduction can be interpreted by the decrease in the effective magnetic field because of the antiferromagnetic coupling between the conduction electrons and localized Fe magnetic moment [26]. Thus, the Fe impurities affect the spin of the conduction electron carriers. We also evaluate $\lambda_u$ by another method (intercept method) comparing the amplitudes of $\beta$ oscillations for each sample (see Supplementary Section 2 and Fig. S3). The estimated values from the intercept method are 0.608$\pi$ and 0.589$\pi$ for Fe1 and Fe2, respectively. $\lambda_u$ values obtained from the two methods are consistent. The intercept method is alternatively useful when the harmonics method is difficult to apply.

Next, we discuss how the Fe impurities affect $\lambda_u$. We assign values $2\pi(N + 1/4)$ and $2\pi(N/2 + 1/4)$ to the minima and maxima of the oscillations and plot $N - 1/B_{extrema}$ (Landau fan diagram), where $N$ is a positive integer. In the plot, the $N$-intercept $\gamma$ manifests the phase offset by $2\pi\gamma = -\pi + \frac{\pi}{2}(1 - \text{sign}(\cos \lambda_u)) + \lambda_u + \delta$ from Eq. (1). Since the $\lambda_u$ values are in the $[0.5\pi, \pi)$ range in our samples, $\gamma$ becomes $(\lambda_u + \delta)/2\pi$. In Fig. 3, the Landau fan diagrams show that the slopes for pristine NbSb$_2$, Fe1, and Fe2 are almost identical, but the values of intercept increase with the Fe doping ratio, which are $-0.192$, $-0.163$, and $0.103$, respectively. From the intercepts, we estimate $\lambda_u + \delta$ as $-0.384\pi$, $-0.326\pi$, and $0.206\pi$ for pristine NbSb$_2$, Fe1, and Fe2, respectively. The value of pristine NbSb$_2$ is close to $-0.250\pi$, which originates from the zero phase added by the phase of the maximum orbit in three-dimensional Fermi surface $-0.250\pi$. The small deviation from $-0.250\pi$ can be caused by the error from the superconducting magnet’s remanent field. If the remanent field error is small compared to the applied field, the phase error is given by a simple power expansion $-2\pi F\Delta B/B^2$. Assuming that the remanent field error is about 10 G, a phase error of about $-0.06\pi$ can arise, whose size is similar to the phase deviation from $-0.250\pi$. The phase deviations from the phase of pristine NbSb$_2$ for Fe1 and Fe2 are $0.058\pi$ and $0.590\pi$, respectively. This indicates that the phase deviation is large in the high-doped sample Fe2. For the low-doped sample Fe1, the phase is almost the same as that of pristine NbSb$_2$. This change can be attributed to the TRS broken by the paramagnetic Fe
impurities. Generally, for materials with TRS, $\lambda_s = 0$, and the observed phase is discretized to $\delta$ or $\delta + \pi$ by
\[
\frac{\pi}{2} \{1 - \text{sign}(\cos \lambda_{as})\} + \delta.
\]
If a system has a broken TRS, the phase deviates from those two values by nonzero $\lambda_s$, which is the anomalous phase.

The anomalous phase is related to the tilting of spins at the Fermi surface, which is attributed to the SOC. Fig. 4 shows how the SOC and broken TRS affect $\lambda_{as}$ and $\lambda_s$. Herein, we assume that the TRS is preserved or perturbatively broken so that the system can be viewed as almost spin degenerate. First, we start without the SOC. In this case, no reason exists for the tilting of spins because the eigenstates are defined as parallel or antiparallel states along with the applied magnetic field [Fig. 4(a)]. The size of Zeeman splitting divided by the magnetic field determines $\lambda_{as}$, and it determines the amplitude of oscillation as $|\cos \lambda_{as}|$. If the SOC is turned on, the eigenstates are affected by the crystal momentum. Moreover, an orbital magnetic moment is introduced by the SOC [Fig. 4(b)]. With TRS, the average magnetic moments of spin up and down are symmetrically tilted. If the TRS is broken with the SOC, the average magnetic moment of the spin up and downs are asymmetrically tilted, inducing asymmetric energy-level splitting [Fig. 4(c)]. In this case, the energy-level splitting is symmetric about the new center energy level [sky blue line in the upper panel of Fig. 4(c)]. The difference between the new center and the original center determines $\lambda_s$, and it causes the anomalous phase in the oscillations [see the lower panel of Fig. 4(c)]. As shown in Fig. 4, similar to the anomalous Hall effect, the anomalous phase requires both broken TRS and SOC. The anomalous phase indicates the polarization extent of a conduction electron by the broken TRS. Therefore, it can provide essential information about the behavior of conduction electrons on magnetic structures.

In summary, we analyze the MQOs of pristine and Fe-doped NbSb$_2$ single crystals. We show that the anomalous phase is observed in the Fe-doped samples and demonstrate that it is attributed to the broken TRS and SOC, like the anomalous Hall effect. Furthermore, the anomalous phase is useful to study magnetic materials, and it has a distinct advantage. In the Hall effect, the anomalous and normal Hall effects are mixed and detected together as a Hall voltage. On the one hand, the anomalous Hall phase can be easily separated from the normal phase, which is discretized to $\delta$ or $\delta + \pi$. Furthermore, it is more sensitive to time-reversal breaking by impurities. Since the electrons in the vicinity of the Fermi surface are most strongly scattered by impurities, magnetic impurities sensitively affect the anomalous phase of MQOs. Thus, we anticipate that the anomalous phase will be actively used to investigate interesting and various magnetic systems.
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FIG. 1. The temperature-dependent magnetic susceptibilities of pristine NbSb$_2$ and Fe-doped NbSb$_2$ (Fe1–Fe4). The inset shows the temperature-dependent inverse magnetic susceptibilities (the open circles) and the Curie–Weiss fitting lines (the solid lines). Estimated Fe doping ratios from the fitting are 0.18% and 0.52% for Fe3 and Fe4, respectively, assuming that the valency of Fe is Fe$^{3+}$. The background susceptibilities from the fitting are $\chi_0 \sim -6.4 \times 10^{-5}$ and $0.1 \times 10^{-5}$ emu/mol-Oe for Fe3 and Fe4, respectively. The labels of the inset figure are omitted if they are the same as those of the main figures.
FIG. 2. The properties of MQOs for pristine and Fe-doped NbSb$_2$. (a) The field-dependent magnetization at a high field range (5.5~7 T). The inset shows the magnified curve for Fe3. (b) The FFT data of the MQOs. We conduct FFT for the MQOs in the range of 5~7 T. $\zeta$, $\alpha$, $\beta$, and $2\beta$ (the second harmonics of $\beta$) oscillations are defined. The yellow area is the FFT band-pass filter range used for extracting $\beta$ oscillations. The inset shows the magnified curve for Fe3.
FIG. 3. The Landau fan diagram of pristine and Fe-doped NbSb$_2$. We assign $2\pi(N + 1/4)$ and $2\pi(N/2 + 1/4)$ to the minima and maxima of the oscillations and plot $N - 1/B_{\text{extrema}}$ (the open symbols), where $N$ is a positive integer. The solid lines are linear fitting lines. The inset shows the magnified intercepts of the fitting lines. The labels of the inset figure are omitted if they are the same as those of the main figures.
FIG. 4. The illustration for the energy levels of orbits (upper panel) and corresponding MQOs (lower panel). The black solid line is the energy level before the Zeeman splitting. The red and blue solid lines in the upper panel are the energy levels of spin up and down orbits, respectively. The red and blue arrows manifest the average magnetic moment of the orbits (upper panel). The red and blue dashed lines are the oscillations from the spin up and down orbits, respectively, and the black solid lines in the lower panel are the total oscillations observed. (a) The case without SOC. The green arrow in the upper panel indicates that the energy difference of the orbits is proportional to $\lambda_{s}$. The green arrow in the lower panel denotes that the amplitude of the MQO is proportional to $\cos \lambda_{s}$. (b) The case with SOC and TRS. (c) The case with SOC but without TRS. The sky blue solid line and arrow in the upper panel manifest the shifted energy center and corresponding $\lambda_{s}$. The sky blue arrow in the lower panel shows the anomalous phase $\lambda_{s}$. 
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