Time Reversal Symmetry Breaking in the B Phase of the Heavy Fermion Superconductor PrOs$_4$Sb$_{12}$

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We present polar Kerr effect measurements of the filled skutterudite superconductor PrOs$_4$Sb$_{12}$. Simultaneous AC susceptibility measurements allow us to observe the superconducting transition under the influence of heating from the optical beam. A nonzero Kerr angle $\theta_K$ develops below the superconducting transition when trained by a small magnetic field, saturating at $\sim 300$ nrad at low temperatures. By extrapolating the measured $\theta_K(T)$ to zero optical power, we are able to show that the Kerr angle onset temperature is consistent with the transition to the B phase at $T_{C2}$. Our results indicate that the order parameter in the B phase breaks time reversal symmetry.

Besides unconventional superconductivity, chiral superconducting phases exhibited by a handful of heavy fermion (HF) materials have recently attracted heightened interest as hosts for Majorana particles and other topologically ordered states [1–3]. Of these, the filled skutterudite PrOs$_4$Sb$_{12}$ has been proposed as a leading candidate for hosting three-dimensional Majorana fermions [4]. PrOs$_4$Sb$_{12}$, to date the only known Pr-based HF-superconductor [5], has been shown to exhibit a number of interesting phenomena [6], including a field-induced ordered state [7] and two superconducting phases at zero field—an A phase with $T_{C1} \approx 1.85$ K, and a B phase with $T_{C2} \approx 1.7$ K [8, 9]. Past experiments have suggested that quadrupolar order and fluctuations may be the basis of all of these phases [5, 6, 10]. Theoretical models posit that such a quadrupolar superconducting state breaks time-reversal symmetry (TRS) and that the double transition arises from spin-orbit coupling [11]. A muon spin relaxation study of PrOs$_4$Sb$_{12}$ showed evidence of TRS breaking (TRSB) appearing around the superconducting transition temperature, thus suggesting that the superconductivity is chiral, but was unable to resolve whether TRSB was associated with the A phase or B phase [12]. Whether the two transitions are in fact distinct, and what are the possible symmetries allowed for this compound, are still subjects of considerable debate [6, 10, 13]. It is thus crucial to determine the exact TRS of both superconducting states.

In general, a TRSB order parameter with particle-hole asymmetry will lead to complex indices of refraction for right-circular ($n_R$) and left-circular ($n_L$) polarizations that are unequal and depend on the direction of propagation of light [14]. This generates a small but finite polar Kerr effect (PKE), wherein linearly polarized light, incident normally on a TRSB medium, is elliptically polarized and phase-shifted upon reflection; the degree of rotation of the major axis of the reflected polarization state relative to that of the incident beam is called the Kerr angle $\theta_K$. Equivalently, right- and left-circularly polarized light exhibit a relative phase difference of $2\theta_K$ when reflected from a TRSB material [15]. For a multiband, TRS-breaking superconductor with $T_c \sim 1$ K measured with visible light or near-IR light, we expect $\theta_K \approx 0.1 – 1 \mu$rad, depending on materials parameters [16]. Such a small PKE may be resolved using a zero-area loop Sagnac interferometer (ZALSI) as described previously [17, 18]. Our ZALSI apparatus is designed to yield a finite phase shift only if TRS is broken, while rejecting any reciprocal effects that may happen to rotate the polarization of the light. Since if reciprocity holds the Kerr effect is identically zero [19], a finite Kerr effect is an unambiguous determination of TRSB in any material system, including unconventional superconductors. Indeed, we have used ZALSI in the past to detect TRSB in Sr$_2$RuO$_4$ and in the HF-superconductors URu$_2$Si$_2$ [20] and UPt$_3$ [21].

In this Letter we report polar Kerr effect measurements of PrOs$_4$Sb$_{12}$ along the [001] direction using a ZALSI apparatus constructed to work at a wavelength of 1.55 $\mu$m [17]. In-situ AC susceptibility measurements allow us to track the superconducting transitions to the A and B phases under the influence of the optical beam and thus accurately account for optical heating. We find a finite Kerr angle, saturating at $\sim \pm 300$ nrad at low temperature, which develops below the superconducting transition temperature after the sample has been cooled down in a small symmetry-breaking magnetic field. By measuring the power dependence of the temperature at which the Kerr angle departs from 0, we are able to extrapolate to the true temperature of TRSB in the limit of no sample heating, which we find is consistent only with $T_{C2}$. We further find that the temperature dependence of the Kerr angle is better fit by a two-component model (i.e. one which assumes that only the B phase breaks TRS) than a one-component model (in which the real
and imaginary components of the order parameter onset in the A phase). We thus conclude that the B phase of superconductivity in PrOs$_4$Sb$_{12}$ breaks TRS.

The approximately 1 × 1 mm$^2$ × 0.3 mm-thick single crystal of PrOs$_4$Sb$_{12}$ was grown in an Sb flux as described in Ref. [22]. X-ray diffraction measurements [5] on PrOs$_4$Sb$_{12}$ reveal that it crystallizes in the LaFe$_3$P$_{12}$-type BCC structure with a lattice parameter $a$ = 9.3017 Å[23]. These crystals typically have a residual resistivity ratio $\rho(300\,K)/\rho(2\,K)$ ≈ 30 – 50 [5, 6, 24]. The sample is attached to a thin sapphire wafer on top of a copper stage away from the beam. This indicates that the temperature of the spot that will be rele-

vant for our analysis, as the Kerr measurement samples the sample as would be expected for a focused heating spot. It is the temperature of this spot that will be relevant for our analysis, as the Kerr measurement samples over the volume that the beam interacts with.

The double-transition shape of the curve is located just underneath the sample, as shown in the inset of Fig. 1. We drive the outer coil at 10.054 kHz and measure the induced voltage in the pickup. The pickup coil is nominally balanced to provide zero signal when the sample susceptibility $\chi$ is zero and finite signal when $\chi$ is finite. In practice there is always some background signal; we measure this offset well above $T_{C1}$ and subtract it from our data. We are able to measure with the optical beam on, thus determining the effect of sample heating from our optical measurement.

PKE measurements of PrOs$_4$Sb$_{12}$ proved to be challenging because of the poor reflectivity of this material at the measurement wavelength ($\lambda$ = 1.55µm). However, signal to noise could be increased by using higher optical power, which in turn resulted in local heating of the sample. Thus, to get reliable data in the limit of low optical power we used a well controlled protocol by which PKE was measured at different optical powers and was then compared to AC susceptibility measurements that were taken with the same optical power turned on. Measurements of the superconducting transition under illumination at different optical powers are shown in Fig. 1. With the optical beam off, we observe two superconducting transitions in the real component of the susceptibility $\chi'$ beginning at 1.83 K and 1.7 K. These values are consistent with $T_{C1}$ and $T_{C2}$ from previously reported measurements of PrOs$_4$Sb$_{12}$ [6, 10]. With the optical beam on, both transitions shift to lower temperature as measured by a RuOx thermometer mounted to the sample stage away from the beam. This indicates that the sample is heated by the beam and thus sits at higher temperature. The double-transition shape of the curve remains unchanged, although at high powers (e.g. the 30 µW data shown), a hint of the original transition at 1.83 K may be seen, presumably due to uneven thermalization of the sample as would be expected for a focused heating spot. It is the temperature of this spot that will be relevant for our analysis, as the Kerr measurement samples over the volume that the beam interacts with.

To fit the MI data, we use the canonical form of susceptibility of a cylinder in a parallel field,

$$\chi' \sim - \left[ 1 - \frac{2\lambda}{R} \frac{I_1(R/\lambda)}{I_0(R/\lambda)} \right]$$

where $R$ is the radius of the cylinder, $\lambda$ is the penetration depth, and $I_n$ are the modified Bessel functions [25]. We then sum the susceptibilities due to two different superconducting states, $\chi = \sum_i \chi(\lambda_i)$, using a phenomenological temperature dependence for penetration depths

$$\lambda_i = (1 - (T/T_{C_i})^4)^{-1/2}$$

The exact shape of these fits seems unimportant, as the $T_{C_i}$ values extracted from them does not depend strongly on the choice of functional form; however, a two-transition fit is necessary to capture the shape of the data. The $T_{C}$ values extracted from fitting agree with the estimates “by eye” of the beginnings of the transitions. We may thus use these temperatures to determine what state the sample is in at a given temperature for the Kerr measurements.

PKE measurements were performed with the MI drive turned off to prevent any spurious effects from the AC magnetic field. The measurement procedure is thus: the sample is first warmed far above the superconducting
transition, typically to 4 K. After a short wait for thermalization, a small DC magnetic field may be applied to train the sample, or the field may be left at zero. The sample is then cooled to base temperature (∼300 mK) and the field is set to 0 (remanent field in the absence of applied field is less than ∼3 mG [20]). Finally, the sample is warmed slowly and PKE measurements are performed during the warm-up.

PKE data taken during zero field cooldowns at different powers are shown in Fig. 2(a). For most cooldowns there is no statistically significant deviation from $\theta_K = 0$. On occasion we will observe a small signal at the lowest temperatures under low power. This behavior, together with the finite-field cooldown measurements discussed below, suggest that we observe the effect of finite domain structure. Similar to a finite size ferromagnet, the TRSB sample may break into domains that are much smaller than the gaussian waist of our optical beam. In such a case the average Kerr effect is expected to be zero, with a standard deviation that reflects the ratio of the domain size to the beam size [26]. Occasionally a large domain may form directly under the beam, leading to a finite signal, but this measurement will not be repeatable.

Again in analogy to a ferromagnet, the sample can be trained to form a single domain by cooling it down through the TRSB transition in a small symmetry-breaking magnetic field perpendicular to the plane of incidence of light [26]. It is important to note, however, that the field is removed at low temperature, and all data are taken warming up in zero field. Data taken at 10 $\mu$W optical power after cooling in field are shown in Fig. 2(b). A nonzero $\theta_K$ develops below ∼1.4 K at all fields, and saturates at ∼±300 nrad at low temperature. The sign of $\theta_K$ reverses with the field direction, as would be expected for trained TRSB. The magnitude of $\theta_K$ shows no field dependence, indicating that vortex cores are unlikely to be the source of finite measured Kerr angle and that a field of 50 G is sufficient to fully train the sample.

Since $\theta_K$ does not depend on cooldown field strength and is symmetric about zero, we may average together curves at various cooldown fields, simply multiplying those at negative fields by −1. Averaged data taken at 10 $\mu$W incident power are shown in Fig. 3. We see a clear deviation from $\theta_K = 0$ at ∼1.4 K. To more precisely determine the temperature $T_K$ at which the Kerr angle becomes nonzero (i.e. at which TRSB begins) we fit the data to two phenomenological models. The first (dashed green line) assumes a single component to the order parameter:

$$\theta_K(T) \sim (1 - (T/T_K)^2)$$

The second (solid blue line) assumes two components to the order parameter, i.e. two critical temperatures:

$$\theta_K(T) \sim \sqrt{(1 - (T/T_K)^2)(1 - (T/(T_K + \Delta T))^2)}$$

Here, $\Delta T = T_{C1} - T_{C2}$ is the difference between the superconducting transition temperatures at this optical

![FIG. 2. (color online) (a) Kerr angle as a function of temperature at three different powers after cooling in zero magnetic field. Error bars represent statistical error of hundreds of data points averaged together. No clear deviation from zero may be resolved, especially at higher powers where the data stay clearly around $\theta_K = 0$. (b) Kerr angle at 10 $\mu$W power after cooling in various fields. A nonzero $\theta_K$ develops symmetrically below ∼1.5 K, saturating at roughly 300 nrad. The magnitude of the signal appears independent of field strength.](image)

![FIG. 3. (color online) Averaged Kerr data taken at 10 $\mu$W incident power. Error bars are statistical error (one-σ). Fits with two critical temperatures (solid blue line) or one (dashed green line) are overlaid, with the two-component fit more closely tracking the data.](image)
power as measured by MI. The two-component fit more closely fits our data, giving $T_K = 1.471 \pm 0.044$ K, where the error bar indicates the 95% confidence interval. Note that this is lower than the temperatures of both superconducting transitions (measured to be 1.715 and 1.563 K at this power); this is to be expected in the presence of optical heating, as the Kerr measurement samples only the volume heated by the optical beam while the MI measurement averages over the larger volume of the sample. A finite element model of optical heating gives a “hot spot” which is 100 – 300 mK hotter than the rest of the sample, consistent with our results. Even with the discrepancy in temperatures, the closer fit provided by the two-component model is evidence that TRSB begins in the B phase.

In order to precisely determine the true value of $T_K$ (i.e. the value that would be measured if heating was eliminated) we measure Kerr data as a function of incident optical power ($P$) and extract $T_K(P = 0)$ from two-component fits as above. The results are shown in Fig. 4, along with measured transition temperatures at each power. We fit a linear dependence to $T_K(P)$ from $P = 5$ to 20 $\mu$W; at the highest power, 30 $\mu$W, we expect some deviation from a linear dependence as the thermal conductivities of the sample and stage have changed significantly. The linear fit intercepts $P = 0$ at $T_K = 1.688 \pm 0.074$ K. Again, the error bars represent 95% confidence bounds. Thus, we see that the Kerr angle begins developing at a temperature that is completely consistent with $T_{C2} = 1.7$ K and inconsistent (at the 3.8-$\sigma$ level) with $T_{C1} = 1.83$ K. We take this as evidence that the B phase breaks TRS while the A phase does not.

In conclusion, we have found a finite polar Kerr effect in the B-phase of the superconducting state of PrOs$_4$Sb$_{12}$. The very small (consistent with zero) PKE after cooling in zero field, together with a finite Kerr angle observed after training the sample through the transition with a small magnetic field, suggest that time-reversal symmetry is broken in PrOs$_4$Sb$_{12}$, with typical domain size that is much smaller than our $\sim 10 \mu$m optical spot. This finding puts strong constraints on the possible symmetries allowed to describe the superconducting state in this material system.

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![FIG. 4. (color online) Measured values of $T_{C1}$ (orange circles), $T_{C2}$ (light green circles), and $T_K$ (blue squares) as a function of optical power. Error bars indicate 95% confidence intervals on the values of $T_K$ extracted from Kerr data. The dashed line is a linear fit to $T_K(P)$ from 5 – 20 $\mu$W. This extrapolates back to a value $T_K(0) = 1.688 \pm 0.074$ K (white square), which is consistent with $T_{C2}$.](image-url)

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