Unconventional Pairing State in Weakly Correlated Non-centrosymmetric Superconductors

J Chen, H Q Yuan
Department of Physics, Zhejiang University, Hangzhou, Zhejiang 310027, China
E-mail: hqyuan@zju.edu.cn

Abstract. We briefly review the recent progress on the study of weakly correlated non-centrosymmetric (NCS) superconductors, with an emphasis on their novel pairing symmetry and the upper critical field arising from the absence of inversion symmetry. Measurements of penetration depth, specific heat, NMR, etc., have shown that non-BCS-like superconductivity with a nodal gap structure may appear in simple metallic NCS superconductors, which allows the admixture of spin-singlet and spin-triplet pairing states attributed to the antisymmetric spin-orbital coupling (ASOC). Furthermore, large upper critical field with a value exceeding the Pauli paramagnetic limit was also experimentally observed in NCS superconductors.

1. Introduction
The symmetries of a superconductor, e.g. time-reversal and spatial inversion symmetry, may impose important constraints on the pairing states. Most of the previously investigated superconductors possess an inversion center. According to the Pauli principle and parity conservation [1,2], their Cooper pairs are either in an even-parity spin-singlet or odd-parity spin-triplet pairing state.

However, the tie between spatial symmetry and the Cooper-pair spins might be violated in a superconductor lacking inversion symmetry [3-7]. In these materials, an asymmetric potential gradient yields an antisymmetric spin-orbit coupling (ASOC), which breaks the spin degeneracy and allows for the admixture of spin-singlet and spin-triplet in the superconducting pairing states [5,7]. The ratio of spin-triplet to spin-singlet contribution might strongly depend on the ASOC strength. The spin-triplet pairing state may significantly contribute to the superconducting gap function when the ASOC strength is larger than the superconducting energy scale [8]. Unconventional behavior, including nodal superconducting gap, is then possible, even if the pairing wave function exhibits the full spatial symmetry of the crystal.
Non-centrosymmetric (NCS) superconductivity has been found in quite a few heavy-fermion (HF) compounds, e.g., CePt$_3$Si, CeIrSi$_3$ and CeCoSi$_3$. In CePt$_3$Si, the observation of a pronounced coherence peak in $1/T_1T$ vs. $T$ just below $T_c$, together with a power-law temperature dependence of the penetration depth and $1/T_1T$, strongly suggests an admixture of spin-singlet and spin-triplet pairing states [9-11]. Furthermore, a huge upper critical field, which well exceeds the Pauli limit in a weak-coupling BCS model, was observed in CeIrSi$_3$ [12] and CeCoSi$_3$ [13]. These unconventional properties were tentatively interpreted in terms of a Rashba-type ASOC model arising from the absence of inversion symmetry. Unfortunately, the nature of superconductivity is complicated by its coexistence with magnetism as well as the strong correlation effects in the NCS HF systems, in which spin fluctuations may cause unconventional superconductivity. Weakly correlated NCS systems with a tunable spin-orbital coupling strength are, therefore, highly desired in order to reveal the effect of broken inversion symmetry on superconductivity.

In recent years, a series of NCS superconductors which show simple metallic normal state without any hint of magnetic ordering or strong electronic correlations have been synthesized [14-16]. Unfortunately, most of these compounds exhibit BCS-like superconductivity, and therefore, did not attract considerable attention. However, observation of a spin-triplet state in an s-wave-like superconductor Li$_2$Pt$_3$B, has largely stimulated the study of superconductivity lacking inversion symmetry [17]. Until now, unconventional superconducting features, e.g., a nodal gap structure and/or a large upper critical field, have been shown in quite a few weakly correlated NCS superconductors, including Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B [18], Y$_2$C$_3$ [19], Mo$_2$Al$_2$C [20] and Mg$_{10}$Ir$_{19}$B$_{16}$ [21]. These compounds might present good examples for studying the effect of ASOC on superconductivity and the related phenomena as well as guidance for further search of potential NCS superconductors which might show novel properties. In this article, we will concentrate on the unique properties of a few simple metallic NCS superconductors, in which the magnetic fluctuations and strong electron-electron correlations are ruled out as a pairing channel for unconventional superconductivity.

2. Superconducting pairing symmetry

![Figure 1. Temperature dependence of (a) the penetration depth $\Delta\lambda$ [17] and (b) $^{11}$B Knight shift [22] for Li$_2$Pd$_3$B and Li$_2$Pt$_3$B. The solid and dashed lines below $T_c$ in (b) are fittings to the BCS theory with $\Delta_0=1.1k_BT_c$.](image-url)
Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B crystallizes in a cubic structure (space group P4$_3$32) and shows simple metallic behavior above $T_c$. Measurements of the penetration depth [17], NMR [22] and specific heat [23] have shown that Li$_2$Pd$_3$B is a BCS-like superconductor, but Li$_2$Pt$_3$B behaves like a spin triplet superconductor. Penetration depth measurement using a tunnel diode (TDO)-based resonant oscillator is a powerful tool to look into the superconducting order parameter. Very remarkably, the sister compounds of Li$_2$Pd$_3$B and Li$_2$Pt$_3$B shows sharply distinct behavior of the penetration depth at low temperature (see Figure 1(a)) [17]. In Li$_2$Pd$_3$B ($T_c$=6.7K) $\lambda(T)$ shows BCS-like exponential behavior, while it follows a linear temperature dependence in Li$_2$Pt$_3$B ($T_c$=2.3K) which indicates the existence of line nodes in the energy gap [17]. It was shown that the dramatically different behavior between Li$_2$Pd$_3$B and Li$_2$Pt$_3$B can be described by a model based on the ASOC which admixes the spin-singlet and spin-triplet pairing state. In Li$_2$Pd$_3$B, the ASOC is weak, and therefore, the spin-singlet state dominates over the spin-triplet state, giving rise to the fully gapped BCS-like behavior. With increasing the ASOC strength in Li$_2$Pt$_3$B, the spin-triplet contribution becomes dominant, leading to a nodal gap structure. These findings were later confirmed by the NMR experiments [22]. Temperature dependence of the $^{11}$B Knight shift is shown in Figure 1(b) for Li$_2$Pd$_3$B and Li$_2$Pt$_3$B, respectively. While the Knight shift shows an increase below $T_c$ in Li$_2$Pd$_3$B (i.e., a decrease of the electronic spin susceptibility $\chi_e$ due to the negative hyperfine coupling), it remains unchanged when crossing the superconducting transition in Li$_2$Pt$_3$B; the latter provides strong evidence for the existence of spin triplet state in Li$_2$Pt$_3$B.

Figure 2. (a) The normalized superfluid density $\rho_s(T)$ of Y$_2$C$_3$ derived from different experiments [19]. The inset shows $\rho_s(T)$ in the low-temperature region and the solid lines present the fittings based on a two-gap model. (b) The spin-lattice relaxation rate $1/T_1$ versus temperature [26].

The non-oxide transition metal sesquicarbides $M_2$C$_3$ ($M$=La,Y) with a cubic Pu$_2$C$_3$-type structure (space group $\not\Gamma 43d$) presents another important family of NCS superconductors with a relatively high $T_c$ (~18K) [24]. Resembling the Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B system, $M_2$C$_3$ shows no evidence of strong electron correlations and/or magnetic order that could lead to unconventional superconductivity. It was found that, at temperatures near $T_c$, a two-gap BCS model can well describe the superfluid density $\rho_s(T)$ derived either from the TDO-based technique [19] or the $\mu$SR experiment [25] (Figure 2(a)). However, such a fitting is clearly violated at low temperatures. Instead of an exponential behavior expected for a BCS-type superconductor, both the penetration depth $\lambda(T)$ and the corresponding superfluid density $\rho_s$
follows a weakly linear temperature dependence at $T\ll T_c$ [19], suggesting the existence of a nodal gap structure as observed in Li$_2$Pt$_3$B and the partially Pd-substituted compounds [18]. Moreover, the suppression of the Hebel-Slichter peak at $T_c$ in the NMR experiments, together with a power law behavior of $1/T_1 \sim T^3$ at $T<3K$, further supports the existence of line nodes in the energy gap [26].

Mo$_3$Al$_2$C crystallizes in a cubic $\beta$-Mn (A13) structure (space group P4$_1$32) and lacks inversion symmetry in all crystallographic directions. Figure 3 plots the electronic specific heat $C_{el}(T)/T$ versus $T^2$ for Mo$_3$Al$_2$C, showing a sharp superconducting transition at 9K [20]. Observation of a power law behavior $C_p(T) \sim T^3$ below $T_c$ (3K$<T<9K$), instead of exponential behavior, strongly indicates non-BCS-like superconducting behavior in Mo$_3$Al$_2$C. Similar evidence also comes from the NMR experiments [20]. In figure 3(b), the $^{27}$Al-NMR relaxation rate $1/T_1$ is plotted as a function of temperature in a log-log scale, which shows absence of the Hebel-Slichter peak and a power law temperature dependence of $1/T_1 \sim T^n$. All these experimental facts suggest that Mo$_3$Al$_2$C behaves different from a simple BCS-superconductor and it may bridge the BCS superconductor and the spin-triplet superconductor as found in Y$_2$C$_3$ because of their relatively weak ASOC strength.

**Figure 3.** (a) Electronic specific heat $C_{el}(T)$ of Mo$_3$Al$_2$C. The dashed line is a guide for the eye. The solid line represents $C_p(T)$ of a BCS superconductor. (b) Temperature-dependent $1/T_1$ $^{27}$Al NMR relaxation rate deduced at $\mu_0H=1.24T$. The dashed line represents exponential temperature dependence [20].

Observation of a nodal gap structure in simple metallic NCS superconductors is rather intriguing. In these materials, the absence of strong electron-electron correlations and magnetic ordering rule out them as a pairing channel for unconventional superconductivity which was widely discussed in HF systems and the high-$T_c$ cuprates. The ASOC, resulting from the broken inversion symmetry, is regarded as an alternative model to interpret the unconventional superconductivity observed in these NCS compounds. In such a model, the spin-triplet pairing state may significantly contribute to the superconducting gap function even within the framework of conventional phonon pairing mechanism, provided that the ASOC strength is sufficiently large compared to the superconducting gap.

Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B is a very ideal system for studying the effect of ASOC on superconductivity. With increasing the Pt concentration to enhance the ASOC strength, the pairing state changes from a fully gaped spin-singlet to a spin-triplet dominated state with a nodal gap structure. In Y$_2$C$_3$ and Mo$_3$Al$_2$C,
the band splitting due to the ASOC effect is nearly compatible with the superconducting gap, in which case the admixture of spin-triplet and spin-singlet pairing states may lead to a more complicated consequence, resulting in an anisotropic energy gap or even accidental nodes on the Fermi surface. The existence of a spin-triplet pairing state in an s-wave-type superconductor provides an alternative approach to study unconventional superconductivity, including topological superconductivity.

3. Upper critical field

In non-centrosymmetric superconductors, the upper critical field can be considerably enhanced as a result of the ASOC effect. In most of the NCS HF superconductors, e.g., CeIrSi$_3$ [12] and CeCoSi$_3$ [13], the upper critical field is large and well beyond the Pauli paramagnetic limit. However, in the case of weakly correlated NCS superconductors, the behavior of upper critical field $\mu_0 H_{c2}(T_c)$ seems to be more complicated. Even though the pairing state of Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B fundamentally changes with the Pt-doping concentration, it was recently found that the H-T phase diagram for variant Pt-contents is essentially unchanged and their normalized upper critical field $H_{c2}(T)/H_{c2}(0)$ can be scaled by $T_c$ (see Figure 4(a) from Ref. 27). Nevertheless, the upper critical field $\mu_0 H_{c2}(T_c)$ cannot be described in terms of the weak-coupling Werthamer-Helfand-Hohenberg (WHH) method even though its upper critical fields are well below the Pauli limit. In Y$_2$C$_3$ and Mo$_3$Al$_2$C, the zero temperature value of the upper critical field $\mu_0 H_{c2}(0)$ is close to the Pauli paramagnetic limit and its temperature dependence also deviates from the WHH behavior. As an example, in Figure 4(b) we show the upper critical field $\mu_0 H_{c2}(T)$ of Y$_2$C$_3$, which was obtained using a TDO-based resonant oscillator [28]. One can see that the upper critical field increases linearly with decreasing temperature near $T_c$ and shows an upturn curvature at low temperatures. Furthermore, Y$_2$C$_3$ posses a rather high upper critical field of $\mu_0 H_{c2}(0) = 29$T, higher than the orbital limit ($\mu_0 H_{c2}^{orb}(0) = -0.69T_c(dH_{c2}/dT)_{T_c} = 24.5$T) but compatible with the spin paramagnetic limit ($\mu_0 H_{c2}^{sp}(0) = (1.86T/K)T_c = 28.8T$) derived in terms of the weak coupling BCS theory. All these unusual features might indicate the importance of broken inversion symmetry on superconductivity and the related properties, in which the spin-triplet state may enhance the upper critical field.

![Figure 4](image)

**Figure 4.** The H-T phase diagrams for (a) Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B and (b) Y$_2$C$_3$, respectively. The dashed lines in (b) is fitting to the weak-coupling WHH method [27,28].
4. Future perspectives

We have shown that the weakly correlated NCS superconductors are very promising for investigating the role of broken inversion symmetry on superconductivity. In these systems, the superconducting pairing state might be fundamentally changed purely by tuning the ASOC strength due to the broken inversion symmetry. This provides a new approach to tune the electronic state and will stimulate further studies of novel superconductivity beyond the correlated electron systems.

The major classes of weakly correlated NCS superconductors, e.g., Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B and Y$_2$C$_3$, are extremely air sensitive which have largely restricted our access to different experimental techniques. Furthermore, no successful synthesis of high quality single crystals has been reported for these materials owing to the large difference of the vapor pressure among the constituent elements. Searching for new material candidates with a tunable ASOC are highly desired in order to reveal the intriguing properties caused by the absence of inversion symmetry.

On the other hand, non-centrosymmetric superconductors have been theoretically proposed as important candidates to search for topological superconductivity [29,30]. It would be truly worthwhile to look into the topological edge states of NCS superconductors, which are generally induced by spin-orbital coupling and preserve the time reversal symmetry.

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