Multigap superconductivity in sesquicar-bides La$_2$C$_3$ and Y$_2$C$_3$

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A complex structure of the superconducting order parameter in Ln$_2$C$_3$ (Ln = La, Y) is demonstrated by muon spin relaxation ($\mu$SR) measurements in their mixed state. The muon depolarization rate [$\sigma_c(T)$] exhibits a characteristic temperature dependence that can be perfectly described by a phenomenological double-gap model for nodeless superconductivity. While the magnitude of two gaps is similar between La$_2$C$_3$ and Y$_2$C$_3$, a significant difference in the interband coupling between those two cases is clearly observed in the behavior of $\sigma_c(T)$.

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The revelation of high-temperature superconductivity in magnesium diboride (MgB$_2$, with critical temperature $T_c \simeq 39$ K) has stimulated renewed interest in other boride and carbide superconductors as an alternative path to novel superconductors with an even higher $T_c$ [1]. Sesquicar-bides (Ln$_2$C$_3$, Ln = La, Y) are among such compounds reported in early literatures; they exhibit superconductivity at relatively high critical temperatures ($T_c \simeq 6–11$ K) and their $T_c$‘s strongly depend on carbon composition [2, 3, 4]. Recently, we have found a new superconducting phase in Y$_2$C$_3$ that exhibits a much higher $T_c$ ($\sim 18$ K) comparable with A-15 compounds [5]. This discovery has attracted further attention to the relationship between structural details and superconductivity in sesquicarbide systems. However, despite various attempts [6, 7, 8, 9], little is known so far about the details of superconducting order parameters in La$_2$C$_3$ and Y$_2$C$_3$ from a microscopic viewpoint.

A recent study on the temperature dependence of the nuclear spin-lattice relaxation rate in Y$_2$C$_3$ has suggested the occurrence of multiple superconducting gap with $s$-wave symmetry in a sample having $T_c = 15.7$ K [10]. While similar electronic structure would be expected for La$_2$C$_3$ [9], a report on the specific heat measurement suggests single-gap superconductivity in a specimen with $T_c \approx 13.4$ K [11]. In any case, the real nature of superconductivity in Y$_2$C$_3$ and La$_2$C$_3$, including potential difference between the two systems, still remains largely unclear.

The muon spin rotation ($\mu$SR) technique is a useful microwave tool for probing quasiparticle (QP) density of states available for thermal/field-induced excitation in the mixed state of type II superconductors [12, 13]. The muon depolarization rate in the mixed state is predominantly determined by the magnetic penetration depth ($\lambda$) that is controlled by superfluid density. Since the latter is reduced by the QP excitation, the effective value of $\lambda$ serves as a monitor of the QP excitation. In this letter, we present the result of $\mu$SR measurements on polycrystalline samples of La$_2$C$_3$ ($T_c \sim 11$ K) and Y$_2$C$_3$ ($T_c \sim 15$ K), where a clear sign of double-gap superconductivity is observed in the temperature dependence of the muon depolarization rate. They also provide the first clear case for the double-gap model, where the magnitude of coupling between electronic bands responsible for superconductivity is explicitly examined. Our result establishes a coherent description of multiple band/gap superconductivity in this sesquicarbide system.

For the La$_2$C$_3$ samples, starting materials were prepared by the arc melting method using a mixture of La/Y (99.9 %) and C (graphite, 99.99 %) with stoichiometric composition of sesquicarbide. The obtained Y-C alloys were placed into a BN cell in a dry box under an argon gas atmosphere, and polycrystalline Y$_2$C$_3$ was synthesized by elevating temperature to $1300 \sim 1400$ °C for 30 min under a high pressure of 5 GPa using a cubic-anvil-type equipment. For the polycrystalline La$_2$C$_3$, the La-C alloys obtained by the arc melting were pressed into pellets in a sealed Ta tube, and sintered at 1000 °C for 200 h under a high vacuum condition of $3.0 \times 10^{-5}$ Torr, followed by a slow cooling process to ambient temperature at a rate of 5 °C/h.

The powder x-ray diffraction patterns for both specimens could be indexed as a sesquicarbide phase with the space group of $I\overline{4}3d$. In La$_2$C$_3$, nearly 10% of La$_2$C$_3$ was observed as a minor phase besides that of the sesquicarbide, while Y$_2$C$_3$ was found to be in a single phase. LaC$_2$ behaves as a normal metal above 2 K and only causes a background in the $\mu$SR signal in the superconducting phase. The lattice constants of La$_2$C$_3$ and Y$_2$C$_3$ were determined to be approximately $a = 8.808(5)$ Å and $8.238(5)$ Å, respectively, which are in good agreement with those reported previously [11, 14, 15, 16]. Unfortunately, the precise stoichiometry of carbon has not been determined. Therefore, the chemical composition in this paper refers only to a nominal value. Heat capacity and ac and dc magnetic susceptibilities were measured using MPMSR2 and PPMS (Quantum Design Co., Ltd.,).
is due to the strong electron-phonon coupling rather than the anisotropic Fermi surface or localization effect [11]. We can extract $H_{c2}(0)$ without much uncertainty using the Ginzburg-Landau (GL) theory, $H_{c2}(T) = H_{c2}(0)(1 - (T/T_c)^2)/(1 + (T/T_c)^2)$, where $H_{c2}(0) = \Phi_0/2\pi\xi_{GL}^2$, $\Phi_0$ is the flux quantum, and $\xi_{GL}$ is the GL-coherence length [18]. The best fit using the above equation yields $H_{c2}(0) = 167(3)$ and $256(7)$ kOe for La$_2$C$_3$ and Y$_2$C$_3$, respectively.

Conventional $\mu$SR experiment was performed on the M15 beamline of TRIUMF, Canada. The polycrystalline samples were loaded on a sample holder (a scintillator serving as a muon veto counter, with a sample dimension of $7 \times 7$ mm$^2$) and placed into a He gas-flow cryostat, to which a 100% spin-polarized muon beam with a momentum of 29 MeV/c was irradiated to collect $1.5 \times 10^7$ decay positron events for each spectrum (taking about 1.5 h). Each measurement was performed under a field-cooling process to minimize the effect of flux pinning, and field fluctuation was kept within $10^{-4}$ of the applied field.

Since we can reasonably assume that muons stop randomly on the length scale of the flux-line lattice (FLL), the muon spin precession signal, $\hat{P}(t)$, provides the random sampling of the internal field distribution $B(r)$.

$$\hat{P}(t) = \int_{-\infty}^{\infty} n(B)\cos(\gamma_\mu Bt + \phi)dB,$$

$$n(B) = \langle \delta(B - B(r)) \rangle_r$$

where $\gamma_\mu$ is the muon gyromagnetic ratio ($= 2\pi \times 13.553$ MHz/kOe), $n(B)$ is the spectral density for the internal field defined as a spatial average ($\langle \cdot \rangle$) of the delta function, and $\phi$ is the initial phase of rotation. These equations indicate that the real amplitude of the Fourier transformed muon spin precession signal corresponds to $n(B)$ (except corrections for additional relaxation due to other origins, see below). In the case of relatively large magnetic penetration depth ($\lambda \geq 3000$ Å), $n(B)$ can be well-approximated by a simple Gaussian field profile, yielding $\hat{P}(t) \approx \exp(-\sigma^2t^2/2)\cos(\gamma_\mu Bt + \phi)$, where $\sigma = \gamma_\mu \sqrt{(B - B(r))^2} \propto \lambda^2$ and $B \approx H$ is the mean field. Here, it must be stressed that $\lambda$ is an effective magnetic penetration depth susceptible to the quasiparticle excitation.

Figure 2 shows the time-dependent muon-positron decay asymmetry at 2 K in La$_2$C$_3$ and Y$_2$C$_3$ with their fast Fourier transform (FFT) displayed in the inset. The FFT spectral linewidth in the normal state ($T > T_c$) is determined by the small random local fields from nuclear moments and a limited $\mu$SR time window ($\approx 8$ µs), while that in the superconducting state is further broadened by the formation of FLL and associated inhomogeneous local field distribution $[B(r)]$. The solid curves in the main panels are the best fits of the data in the time domain, assuming two components of the Gaussian damping,

$$A\hat{P}(t) = \sum_{i=1}^{2} A_i \exp\left(-\frac{\sigma_i^2 t^2}{2}\right) \cos(\gamma_\mu B_i t + \phi_i)$$

where the $i$-th component refers to the contribution from superconducting ($i = 1$) and normal ($i = 2$) phases, $A_i$ is the partial asymmetry ($\sum_i A_i = A$), $\sigma_i$ is the relaxation rate, and $\gamma_\mu B_i$ is the central frequency for the respective components. The model yields good fits to data, as indicated by the reasonably small values of reduced chi-square: $\chi^2/N_\nu$ is mostly less than 1.7 for La$_2$C$_3$ and 1.3 for Y$_2$C$_3$, with $N_\nu$ being the number of degrees of freedom. Considering that $\sigma_2$ represents the relaxation due to the nuclear magnetic moment (i.e., $\sigma_2 = \sigma_{20}$), the net relaxation rate in the superconducting state is expressed as $\sigma_1^2 = \sigma_2^2 + \sigma_{2r}^2$, where the second term comes from $n(B)$ in the FLL state and it is proportional to the superfluid density [19]. From the fitting analysis, the superconducting volume fractions $[= A_1/(A_1 + A_2)]$ at 2 K are estimated to be $\approx 0.91$ and 0.98 in La$_2$C$_3$ and Y$_2$C$_3$, respectively, where the former value is in good agreement with the fractional yield estimated by the X-ray analy-
According to the theories that consider multiband superconductors, the applied field below 30 kOe (see the inset of Fig. 3(a)), by the fact that single-gap BCS superconductors. The effect of flux pinning as a possible origin of such structure is ruled out and one electron band (2.73/eV unit cell spin) that arise mainly from the hybridized orbitals of Y d- and C-C antibonding π*-states. Such large differences in the density of states and Fermi velocities between hole and electron bands might lead to the opening of two superconducting gaps in the different parts of the Fermi surface.

The origin of difference in the temperature dependence of σ, between La2C3 and Y2C3 is understood by considering the difference in the interband coupling strength between these two compounds. For quantitative discussion, the data in Fig. 3 are analyzed using a phenomenological double-gap model with s-wave symmetry [24, 25],

\[
\sigma(T) = \sigma(0) - w \cdot \delta \sigma(\Delta_1, T) - (1 - w) \cdot \delta \sigma(\Delta_2, T),
\]

where \( \Delta_i (i = 1 \text{ and } 2) \) is the energy gap at \( T = 0 \), \( w \) is the relative weight for \( i = 1, k_B \) is the Boltzmann constant, \( f(\epsilon, T) \) is the Fermi distribution function, and \( \Delta(T) \) is the standard BCS gap energy. The solid curves in Fig. 3 are the best fit result obtained by using the above double-gap model with the parameters listed in Table I. For La2C3, a simplified model (dashed curve) assuming two independent superconducting bands was also tested against the data, which turned out to exhibit a slightly better agreement than that described by using the above model [yielding \( 2\Delta_1/k_B T_c = 4.5(3) \) and \( 2\Delta_2/k_B T_c = 1.3(3) \)]. This might suggest that the above model may not necessarily be a good approximation for the case of weak interband coupling.

The superconducting parameters deduced from the present experiment are summarized in Table I. Here, we calculated the magnetic penetration depth \( \lambda(0) \) using the formula \( \sigma_v(0) [\mu s^{-1}] = 4.83 \times 10^4 (1 - H/H_{c2}) \times [1 + 3.9(1 - H/H_{c2})^2]^{1/2} / \lambda^2(0) \) [nm] [19, 26]. The gap parameter \( 2\Delta_i/k_B T_c \) of Y2C3 is in reasonable agreement with that deduced by NMR (i.e., \( 2\Delta_2/k_B T_c = 5 \) and 2) [13], again supporting the present double-gap scenario. We also find

### Table I: Superconducting properties of La2C3 and Y2C3 determined from the present experiment, where those obtained from the double-gap analysis correspond to the solid curves in Fig. 3

| Transverse field (kOe) | La2C3 | Y2C3 |
|-----------------------|-------|------|
| \( T_c \) (K)         | 10.9(1) | 14.7(2) |
| \( \sigma_v(0) \) [\mu s^{-1}] | 0.71(3) | 0.48(2) |
| \( \lambda(0) \) (Å) | 3800(100) | 4600(100) |
| \( w \)               | 0.38(2) | 0.86(2) |
| \( \Delta_1(0) \) (meV) | 2.7(1) | 3.1(1) |
| \( \Delta_2(0) \) (meV) | 0.6(1) | 0.7(3) |
| \( 2\Delta_1/k_B T_c \) | 5.6(3) | 4.9(3) |
| \( 2\Delta_2/k_B T_c \) | 1.3(3) | 1.1(5) |
that $2\Delta/k_B T_c$ for the two respective bands of La$_2$C$_3$ are comparable with those of Y$_2$C$_3$. Thus, it appears that the superconductivity of La$_2$C$_3$ and Y$_2$C$_3$ share the common features of strong electron-phonon coupling and s-wave symmetry, which is in line with the previous heat capacity results [11].

Provided that there is a significant difference in the interband coupling between La$_2$C$_3$ and Y$_2$C$_3$, the observed difference in the relative weight ($w$) between two gaps might also be connected with the interband coupling. Furthermore, considering that the double-gap features tend to be suppressed by the localization (scattering) effect, one might suspect that such a difference in $w$ may arise from that in the quality of specimen. In this regard, we have to note that the Y$_2$C$_3$ samples were obtained only in a polycrystalline form using high pressure synthesis and that their short annealing time might have resulted in a quality less than that of La$_2$C$_3$. At this stage, we presume it unlikely that the present result has been strongly affected by the localization effect, considering that the electronic mean free path measured using the microwave cavity perturbation technique is much longer than $\xi_{GL}$ for the sample prepared under the same condition [27]. However, it would be certainly helpful to study the influence of sample quality (and chemical stoichiometry as well) in the future to elucidate the details of the localization effect on the double-gap behavior.

Finally, let us point out the noncentrosymmetric effect in superconductivity. In the case of a sesquicarbides system with the $I\bar{4}3d$ group symmetry, an asymmetric spin-orbit interaction can be approximated by the Dresselhaus-type interaction. When the order of magnitude of a superconducting gap is of comparable to that of the spin-orbit band splitting, the original isotropic gap structure is modulated by a magnetic field to have a point-node, because anisotropic Pauli depairing effect can occur in the specific part of the momentum space [28]. This may lead to unusual field-induced quasiparticle excitation, and a detailed $\mu$SR study on the field dependence of magnetic penetration depth is currently in progress to examine the proposed scenario.

In summary, we performed $\mu$SR experiment on Ln$_2$C$_3$ ($Ln = La$, Y) to clarify the structure of superconducting order parameter through the temperature dependence of quasiparticle excitation reflected in the muon depolarization rate, $\sigma_v(T)$ in the mixed state. We showed that $\sigma_v(T)$ exhibits a characteristic of double-gap in the superconducting order parameter, with a marked variation in the temperature dependence between La and Y compounds that is attributed to the difference in the interband coupling. The gap parameters for two respective bands were deduced using the phenomenological double-gap model and were found to be comparable between La and Y compounds, which is consistent with the occurrence of a strong-coupling superconductivity with s-wave symmetry in both the systems.

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