Multigap Superconductivity in $Y_2C_3$: A $^{13}$C-NMR Study

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We report on the superconducting (SC) properties of $Y_2C_3$ with a relatively high transition temperature $T_c = 15.7$ K investigated by $^{13}$C nuclear-magnetic-resonance (NMR) measurements under a magnetic field. The $^{13}$C Knight shift has revealed a significant decrease below $T_c$, suggesting a spin-singlet superconductivity. From an analysis of the temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ in the SC state, $Y_2C_3$ is demonstrated to be a multigap superconductor that exhibits a large gap $2\Delta/k_BT_c = 5$ at the main band and a small gap $2\Delta/k_BT_c = 2$ at other bands. These results have revealed that $Y_2C_3$ is a unique multigap $s$-wave superconductor similar to MgB$_2$.

KEYWORDS: lanthanoid carbide, metal, superconductivity, multigap, NMR, $Y_2C_3$

The discovery of superconductivity in MgB$_2$, which exhibits a high superconducting (SC) transition temperature $T_c \sim 40$ K, has attracted much interest. Motivated by this discovery, intensive effort is devoted to the search for a new high-$T_c$ material in a similar system that contains light elements B and C. Meanwhile, Amano et al. reported that $Y_2C_3$ prepared under high pressure ($\sim 5$ GPa) is a superconductor with a relatively high $T_c \sim 18$ K, although the superconductivity in this compound was already reported to emerge at $T_c \sim 6–11$ K. As for SC characteristics, the specific heat measurements on the newly synthesized high-purity samples of $Y_2C_3$ have revealed that a gap size of the respective samples with $T_c = 11.6, 13.6,$ and $15.2$ K increases as $2\Delta/k_BT_c = 3.6, 4.1,$ and $4.4$. This result raises a question why $T_c$ and $2\Delta/k_BT_c$ vary significantly depending on sintering conditions. Further systematic experiments are required to gain deep insight into the SC characteristics of this compound.

$Y_2C_3$ crystallizes in the cubic Pu$_2C_3$-type structure (space group $I43d$) without an inversion center, consisting of the dimers of carbon atoms. The SC properties of the sample previously reported by Amano et al. did not exhibit a single SC transition as seen in the inset of Fig. 1(a), pointing to a contamination of extrinsic multiphases. Recently, Akutagawa et al. have succeeded in preparing a single phase of $Y_2C_3$, which enables us to extract intrinsic electronic and SC properties in $Y_2C_3$. From the specific-heat measurements of this sample, the Sommerfeld coefficient $\gamma \sim 6.3$ mJ/mol-K$^2$ and Debye temperature $\theta_D \sim 530$ K were estimated for the sample with $T_c = 15.2$ K. This result suggests that its high Debye temperature makes $T_c$ relatively high despite its small Sommerfeld coefficient. As in MgB$_2$, the light-element constituent like boron and carbon plays a vital role in enhancing $T_c$ in general. In the SC state, the temperature ($T$) dependence of the specific heat exhibits an exponential decrease with $2\Delta/k_BT_c = 4.4$ upon cooling well below $T_c$, suggesting a strong-coupling isotropic superconductivity. From another context, it is noteworthy that a novel SC nature for CePt$_3$Si and Li$_2$Pt$_3$B without inversion symmetry is a recent interesting topic because the admixture of spin-singlet and spin-triplet SC state is shown to emerge due to the spin-orbit coupling. Likewise, determining the order-parameter symmetry and a detailed gap structure is an underlying issue in the newly synthesized high-quality $Y_2C_3$ without inversion symmetry.

In this letter, we report on the SC order-parameter symmetry and gap structure of $Y_2C_3$ with a relatively high $T_c = 15.7$ K ($H = 0$) via $^{13}$C nuclear-magnetic-resonance (NMR) measurements under a magnetic field. $Y_2C_3$ was synthesized by arc melting and high pressure. The sample was confirmed to nearly consist of a single phase by X-ray diffraction analyses, with the formation of a primitive Pu$_2C_3$-type structure. The polycrystalline sample for $^{13}$C-NMR measurement was slightly enriched with $^{13}$C ($^{12}$C : $^{13}$C = 9 : 1) in order to improve the NMR signal-to-noise ratio. $T_c = 15.7$ and $12.2$ K were determined by ac-susceptibility measurements at $H = 0$ and $9.85$ T, respectively. The NMR experiment was performed by the conventional spin-echo method at $H = 9.85$ T in the $T$ range of $1.8 - 70$ K.

Figures 1(a) and 1(b) show the $^{13}$C-NMR spectra of $Y_2C_3$ for the previous sample reported in ref. 2 and the present sample, respectively, in the normal state at $T = 15$ K and $H = 9.85$ T. Note that the spectra for the previous sample are composed of $^{13}$C-NMR signals arising from $Y_3$C, $YC_2$, and $Y_2C_3$, demonstrating the contamination of extrinsic multiphases, whereas the spectra for the present sample consist of a nearly single peak from $Y_2C_3$ with a small contamination of $YC_2$. The NMR intensity for each phase coincides with the x-ray intensity as expected. The full width at half maximum (FWHM) in the $^{13}$C-NMR spectrum of $Y_2C_3$ is as small as 8 kHz, ensuring good sample quality. Actually, a single SC transition at $T_c = 15.7$ K was corroborated by the susceptibility measurement at $H = 10$ Oe as seen in the inset of Fig. 1(b).
Figure 1. (Color online) $^{13}$C-NMR spectra of $Y_2C_3$ for (a) the previous sample reported in ref. 2 and (b) the present sample in the normal state at $T = 15$K and $H = 9.85$T. Note that the spectra for the previous sample are composed of NMR signals arising from $Y_3C$, $YC_2$, and $YC_3$, demonstrating the contamination of extrinsic multiphases, whereas the spectra for the present sample nearly consist of a single peak from $Y_3C_3$ with a small contamination of $YC_2$. The insets of both figures show the $T$ dependence of SC diamagnetic susceptibility down to 4.2K.

Figure 2(a) shows the $T$ dependence of $^{13}$C Knight shift (KS) in $Y_2C_3$, which is determined relative to the resonance frequency of tetramethylsilane (TMS) as a reference substance ($K$ [TMS] $\sim$ 0 ppm). A clear decrease in KS and an increase in FWHM below $T_c$ are indicated in Figs. 2(a) and 2(b), which are derived from the $T$ dependence of NMR spectra as shown in the inset of Fig. 2. In intermediate fields ($H_{c1} \ll H \ll H_{c2}$) where the vortices form a dense lattice, we estimate coherence length and the distance between the vortices to be $d \sim 160 \AA$, and $\xi \sim 34 \AA$, respectively. As a result, a diamagnetic field is led to be $H_{dia} \sim -0.3$Oe using the relation $H_{dia} = -H_{c1} \ln(\beta e^{-1/2}d/\xi)/\ln(\kappa) \sim 3 \times 10^{-4}$% at $H=9.85$T. Here, we used $H_{c1} = 3.3$K.6 The London penetration depth $\lambda = 4470 \AA$, $\beta = 0.381$ for the case of triangular lattice,7 $d \sim 160 \AA$, and $\xi \sim 34 \AA$. Thus, the estimated value of $K_{dia}$ is one order of magnitude smaller than the decrease in KS observed below $T_c$, demonstrating that the decrease in KS is due to the reduction of spin susceptibility associated with the onset of the spin-singlet SC state. If the spin susceptibility was assumed to vanish at low $T$ due to the formation of spin-singlet Cooper pairing, the orbital and spin part of KS are tentatively estimated to be $K_{orb} \sim 0.028$% and $K_s \sim 0.005$%, respectively. A possible cause for the increase in FWHM may be due to an inhomogeneous distribution of vortex lattices, which eventually makes either $d$ or $\lambda$ distribute.

Further systematic NMR measurements at low $H$ are required for inspecting a structure of vortex lattices.

Next, we deal with the $T$ dependence of nuclear spin-lattice relaxation rate ($1/T_1$) in order to clarify the gap structure. The $1/T_1$ for $^{13}$C with nuclear spin $I = 1/2$ is uniquely determined from a simple exponential recovery curve of nuclear magnetization given by the relation $[M(\infty) - M(t)]/M(\infty) = \exp(-t/T_1)$. Here, $M(t)$ and $M(\infty)$ are the nuclear magnetizations at a time $t$ after the saturation pulse and at the thermal equilibrium condition, respectively. Figure 3 presents the $T$ dependence of $1/T_1$ at $H = 9.85$T. In the normal state, the law $T_1/T = const$. is valid down to $T_c$. In the SC state, $1/T_1$ is also precisely measured from a simple exponential recovery curve such as $[M(\infty) - M(t)]/M(\infty) = \exp(-t/T_1)$, as seen in the inset of Fig. 4(a). This is because the possible contribution to $1/T_1$ arising from normal vortex cores is very small, if any, when $\xi \sim 34 \AA < d \sim 160 \AA$.

The inset in Fig. 3 shows $(T_1T)_{const.}/(T_1T)$ vs $T/T_c$ for $Y_2C_3$ at $H = 9.85$T and for MgB$_2$ with $T_c = 29$K at $H = 4.4$T. Here, $(T_1T)_{const.}$ denotes constant values in normal state. In the SC state, we note that a tiny coherence peak is observed in $1/T_1$ just below $T_c$ for $Y_2C_3$ as in MgB$_2$. This is indicative of a full gap opening in $Y_2C_3$ as in MgB$_2$. A reason why the coherence peak is depressed in these compounds may be due to a strong electron-phonon coupling that causes the large life time broadening of quasiparticles induced by thermally excited phonons as reported in ref. 10. In fact, the strong-coupling BCS superconductor such as TlMo$_6$Se$_7$,5 does not show a clear coherence peak.11 Note that the $T$ dependence of $1/T_1$ well below $T_c$ does not exhibit a simple exponential decrease, but seems to have a kink at around $T = 5$K. In order to gain further insight into this unique and relevant relaxation behavior with a possible gap structure in the SC state for $Y_2C_3$, we present in Fig. 4 the Arrhenius plot of $(T_1T)/(T_1T)_{const.}$ vs $T_c/T$. 

with \( T_c = 12.2 \text{ K} \) at \( H = 9.85 \text{ T} \). It is evident that a power-law behavior in \( 1/T_1 \) such as \( 1/T_1 T \propto T^2 \) (see the dashed line in the figure) is not valid at all. Instead, when noting that a line in this plot corresponds to an exponential \( T \) dependence in \( 1/T_1 T \), it is supposed that a large full gap seemingly opens in a high-temperature regime in the SC state, but low-lying quasiparticle excitations in a low-temperature regime are dominated by the presence of a small full gap. In fact, from respective slopes in this plot in the \( T \) range of 5 K-\( T_c \sim 12.2 \text{ K} \) and at temperatures lower than 5 K, gap sizes are estimated to be \( 2\Delta/k_B T_c \sim 5 \) and 2, which suggests that two kinds of SC energy gaps exist, namely, multigap superconductivity takes place in \( \text{Y}_2\text{C}_3 \). We stress that this novel relaxation behavior in the SC state for \( \text{Y}_2\text{C}_3 \) is not due to some inhomogeneous effect originating from the presence of vortex cores and/or a distribution of \( T_c \) because \( 1/T_1 \) is uniquely determined from the simple exponential recovery curve of nuclear magnetization as shown in the inset of Fig. 4. Here, we apply a phenomenological multigap model for nodeless superconductivity to understand the novel relaxation behavior in the SC state. Figure 5 shows the \( T \) dependence of \( 1/T_1 T \). In such a model, \( T_1(T)/T_1(T_c) \) is expressed as

\[
\frac{T_1(T)}{T_1(T_c)} = \frac{\alpha^2}{\alpha^2 + \beta^2} \frac{1}{T_1} (\Delta_\alpha) + \frac{\beta^2}{\alpha^2 + \beta^2} \frac{1}{T_1} (\Delta_\beta),
\]

where \( \alpha \) and \( \beta \) are defined as the respective fractions of \( N(E_F) \times A_{\text{hf}} \) with SC gap \( \Delta_\alpha \) and \( \Delta_\beta \) and \( \alpha + \beta = 1 \).

\( N(E_F) \) and \( A_{\text{hf}} \) are the density of states (DOS) at the Fermi level and the hyperfine coupling constant, respectively. Here,

\[
\frac{1}{T_1} (\Delta) = \frac{2}{k_B T_c} \int_0^\infty dE [N_s^2(E) + M_s^2(E)] f(E)[1 - f(E)],
\]

where \( N_s(E) \) is the DOS, \( M_s(E) \) is the anomalous DOS originating from the coherence effect inherent to a spin-singlet SC state and \( f(E) \) is the Fermi distribution function. Note that \( N_s(E) \) and \( M_s(E) \) are averaged over an energy broadening function assuming a rectangle shape with a width \( 2\delta \) and a height \( 1/2\delta \). We use \( \delta/\Delta(0) = 0.3 \) in the calculation. A theoretical curve based on the multigap model is actually in good agreement with the experiment using \( \beta = 0.75 \) and \( 2\Delta_\beta/k_B T_c = 5 \) for the main band, and \( \alpha = 0.25 \) and \( 2\Delta_\alpha/k_B T_c = 2 \) for other bands as shown by the solid curve in Fig. 5. It is notable that the large gap at the dominant Fermi surface is larger than the weak-coupling BCS value of \( 2\Delta/k_B T_c = 3.5 \), indicating a strong electron-phonon coupling and being consistent with the specific-heat result. The present \(^{13}\text{C}-\text{NMR} \) has revealed that the superconductivity in \( \text{Y}_2\text{C}_3 \) is characterized by a large gap at the main Fermi surface and a small gap at others. This may be consistent with the band calculation which shows the presence of Fermi surfaces consisting of three dimensional multisheets due to the hybridization between \( Y-d \)-derived states and antibonding \( C-d\)-dimers derived \( p\)-states. We should pay attention to the relationship between the multigap and \( T_c \). Although \( \text{Y}_2\text{C}_3 \) is a superconductor with no inversion symmetry, the present experiments have revealed that this noncentrosymmetric compound is a spin-singlet superconductor with full gaps at all the Fermi surfaces, and hence rules out the possibility of the admixture of spin-triplet order parameter which is the recent underlying topic for the superconductors with no inversion symmetry.
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\[ T_1 = \text{const.} \]

\[ T_c = 12.2 \text{ K} \]

\[ Y_2C_3 \quad H = 9.85 \text{ T} \]

\[ T_c = 12.2 \text{ K} \]

Fig. 5. (Color online) \( T \) dependence of \( 1/T_1T \) for \( Y_2C_3 \) with \( T_c = 12.2 \text{ K} \) at \( H = 9.85 \text{ T} \). A phenomenological multigap model for nodeless superconductivity is applied to understand the novel relaxation behavior in the SC state. The solid curve is a theoretical curve based on the multigap model with \( \beta = 0.75 \) and \( 2\Delta_\beta/k_BT_c = 5 \) for the main band, and \( \alpha = 0.25 \) and \( 2\Delta_\alpha/k_BT_c = 2 \) for other band (see the text). The inset shows the \( T \) dependences of the order parameters \( \Delta_\alpha \) and \( \Delta_\beta \).

In conclusion, the superconducting properties of \( Y_2C_3 \) with a relatively high transition temperature \( T_c = 15.7 \text{ K} \) have been investigated using the \( ^{13}\text{C} \) nuclear-magnetic-resonance (NMR) method under a magnetic field. The Knight shift has revealed a significant decrease below \( T_c \), suggesting the spin-singlet superconductivity. The nuclear spin-lattice relaxation study in the SC state has revealed that \( Y_2C_3 \) is a multigap superconductor that exhibits a large gap \( 2\Delta/k_BT_c = 5 \) at the main band and a small gap \( 2\Delta/k_BT_c = 2 \) at others. These results have revealed that \( Y_2C_3 \) is a unique multigap s-wave superconductor similar to MgB\(_2\).

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