^{13}C Nuclear Magnetic Resonance Study of Graphite Intercalated Superconductor CaC$_6$ Crystals in the Normal State

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CaC$_6$ 결정에 대한 정상상태에서의 ^{13}C 핵자기공명 측정

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Abstract

^{13}C NMR (nuclear magnetic resonance) measurements have been performed to investigate the local electronic structure of a superconducting graphite intercalation compound CaC$_6$ (T_c = 11.4 K). A large number of single crystals were stacked and sealed in a quartz tube for naturally abundant ^{13}C NMR. The spectrum, Knight shift, linewidth, and spin-lattice relaxation time T_1 were measured in the normal state as a function of temperature down to 80 K at 8.0 T perpendicular to the c-axis. The ^{13}C NMR spectrum shows a single narrow peak with a very small Knight shift. The Knight shift and the linewidth of the ^{13}C NMR are temperature-independent around, respectively, +0.012% and 1.2 kHz. The spin-lattice relaxation rate, $1/T_1$, is proportional to temperature confirming a Korringa behavior as for non-magnetic metals. The Korringa product is measured to be T_1T = 210 s·K. From this value, the Korringa ratio is deduced to be ξ = 0.73, close to unity, which suggests that the independent-electron description works well for CaC$_6$, without complications arising from correlation and many-body effects.

1. Introduction

Graphite intercalation compounds (GICs) are synthesized by introducing foreign atoms between the 2D sheets of graphite, forming up layered structures.

Because graphite is a semimetal, the electronic properties of graphite are modified by the electrons transferred from the intercalant atoms and changed into a metallic state in GICs.

Superconductivity in GICs has been studied for several decades [1, 2]. Recently the field of GICs has redrawn great attention after the discovery of superconductivity in YbC$_6$ and CaC$_6$ with relatively high transition temperatures, T_c, of 6.5 K and 11.5 K,

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respectively [3]. Among GICs, CaC_6 is exceptional because of its high T_c [3, 4].

The crystal structure of CaC_6 is shown in Fig. 1. The magnetic penetration depth of CaC_6 shows an exponential dependence at low temperature, which supports an s-wave pairing [4, 5]. The electronic specific heat measurements as a function of temperature and field are consistent with a full gap order parameter [6]. According to isotope effect data, superconductivity in CaC_6 is mainly driven by coupling of the electrons by Ca phonon modes [7]. Also the data suggest that the coupling with low energy Ca vibrations must be strong to provide the relatively high T_c. However, the specific heat data are inconsistent and support a weak coupling scenario [8].

Although the vast amount of research results has been reported so far, the superconducting mechanism and the origin are still not fully understood. Then NMR is a microscopic probe, sensitively measuring the local electronic structure at the Fermi energy and the spin dynamics at the probing nuclear site [9]. In addition, NMR is a powerful tool to unveil the spin and the orbital states of cooper pair as well as the gap symmetry. However, no NMR results have been reported yet for CaC_6. Since H_{c2} is small and NMR signal intensity is very weak at small magnetic field below H_{c2}, we performed NMR measurements only in the normal state by using the strong magnetic field of 8.0 T above H_{c2}. Even NMR measurements of electronic structure in the normal state can still provide an important starting point for understanding of the pairing mechanism and the nature of superconductivity. In this paper, we report ^{13}C nuclear magnetic resonance (NMR) measurements to understand the electronic structure in the normal state of CaC_6.

2. Experiments

Single crystal samples of CaC_6 were prepared as described in detail elsewhere [4, 6]. T_c was determined from the temperature dependence of the dc and ac magnetic susceptibilities. The variation of T_c among our samples is less than ~ 0.1 K. All samples show sharp superconducting transition widths $\Delta T_c = \sim 0.15$ K, which is determined from the temperature interval for 10% and 90% of the diamagnetic signal, indicating good sample quality. At ambient pressure, the onset of the superconducting transition of our samples is ~ 11.4 K, consistent with the previous report [2]. Several tens of crystals were stacked together for naturally abundant ^{13}C NMR and sealed into a quartz tube in an argon atmosphere.

The ^{13}C NMR experiments were carried out with a home-made spectrometer and a home-made probe in an 8.0 T superconducting magnet (Oxford, UK) over the temperature range of 80 - 290 K. The ^{13}C NMR spectra were obtained by the fast Fourier transform method by using a spin-echo pulse sequence $(\pi/2-\tau_0-\pi-\tau_0-\text{acquire})$ with a fixed τ_0 value [9]. Typical length of $\pi/2$ pulse was ~10 μs. The spin-lattice relaxation time T_1 was obtained by an inversion recovery pulse sequence by using the spin-echo $(\pi-\tau-\pi/2-\tau_0-\pi-\tau_0-\text{acquire})$ with various τ values [9].
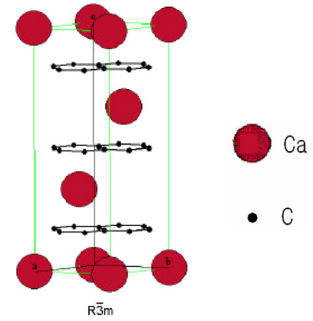

Fig. 1. The hexagonal cell of CaC_6 [Ref. 4].

3. Results and Discussion

Figure 2 is the ^{13}C NMR spectrum at 140 K and 8.0 T perpendicular to the c-axis. The spectrum shows a single narrow peak, as for most nuclei of spin $I=1/2$ in non-magnetic metallic states. The [13]C

NMR Knight shift [10], which is proportional to the density of states at the Fermi energy at the carbon site, is small, +0.012%. This small value of Knight shift is compared with the large value of [63]Cu NMR Knight shift for metallic copper, +0.237% [11]. Thus, the small Knight shift reflects the low density of states at the Fermi energy at the carbon site in CaC_6.

Figure 3 shows the temperature dependence of Knight shift for the ^{13}C NMR. The Knight shift [10] is defined to be $K=(\omega_L-\gamma H_0)/\gamma H_0 \times 100$ (%), where ω_L is the resonant frequency, γ the gyromagnetic ratio of nucleus, and H_0 an external magnetic field.

The Knight shift is measured to be temperature-independent like a Pauli magnetic susceptibility. This is a typical metallic behavior. The Knight shift is a direct measure of the hyperfine field and is proportional to the electron spin density at the nucleus: $K \propto |\Psi_F(0)|^2$, where $\Psi_F(0)$ is the electron wave function at the Fermi energy at the nucleus. In short, $K = \mu_B H_{hf} N(E_F)$, where μ_B is the Bohr magneton, H_{hf} the hyperfine field at the nucleus, and $N(E_F)$ the density of states at the Fermi energy. Since both Knight shift and magnetic susceptibility are proportional to the density of states at the Fermi energy, there is a linear relation between K and χ [10]: for the ^{13}C NMR, $K = K_s + K_p + K_{core} = a_s\chi_s + a_p\chi_p + a_{core}\chi_{core}$, where a is a hyperfine coupling constant and χ_s, χ_p, and χ_{core} are the s-part, the p-part, and the diamagnetic part [12], respectively. The core contribution is usually very small. Also, the s-part is positive whereas the p-part is often negative. Usually $a_s \gg |a_p|$.

The small and temperature-independent Knight shift of CaC_6 is contrasted with the ^{27}Al NMR Knight shift of magnetic RAl_2, such as $CeAl_2$ [13]. The Knight shifts of these samples are huge and strongly temperature-dependent, proportional to the magnetic susceptibility. In such samples, the Knight shifts are dominated by the unfilled *4f* band contribution to the density of states at the Fermi energy.

Figure 4 plots the linewidth of the ^{13}C NMR. The linewidth is narrow, ~1.2 kHz, and temperature-independent. This small and temperature-independent

linewidth is typical for spin I=1/2 nuclei in non-magnetic metals. This linewidth is determined by the nuclear dipole field from neighboring ^{13}C nuclear spins. Therefore, the small and temperature-independent Knight shift and linewidth microscopically confirm that electrons are in a non-magnetic metallic state at the carbon site in CaC_6.
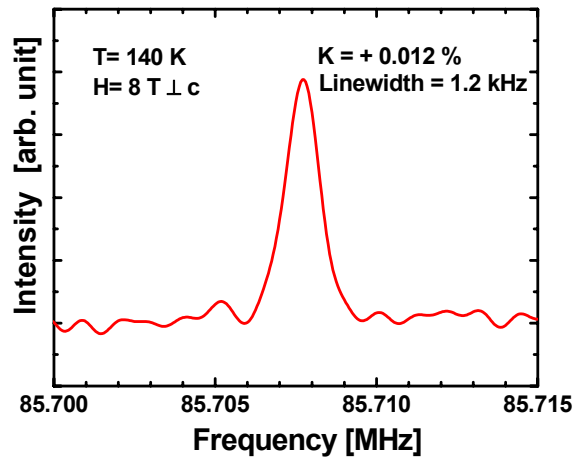
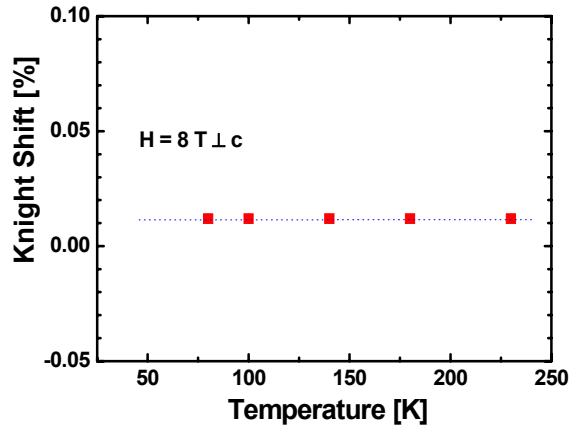Fig. 2. The ^{13}C NMR spectrum at 140 K for field perpendicular to the c-axis.

Fig. 3. Temperature dependence of the ^{13}C NMR Knight shift.

Figure 5 shows a typical spin-lattice relaxation recovery of the ^{13}C NMR. The recovery profile is single-exponential at all temperatures, meaning that

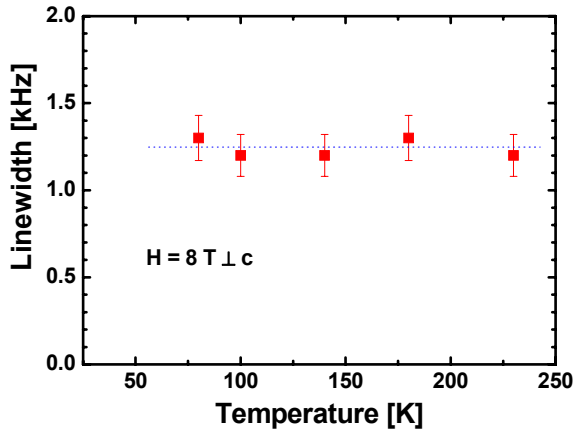one relaxation channel governs relaxation of the ^{13}C nuclear spins.

Fig. 4. Temperature dependence of the ^{13}C NMR linewidth.

The spin-lattice relaxation rate, $1/T_1$, is an energy transfer rate from a nuclear spin system to its surrounding environment, so-called lattice. This energy flow rate is proportional to the coupling strength of nuclear spins to the neighborhood and the quantum excitation probability. In solid samples, the most important channel coupled to nuclei is electrons, so $1/T_1$ is dominated by the spin scattering of conduction electrons and the spin fluctuation of local moments.
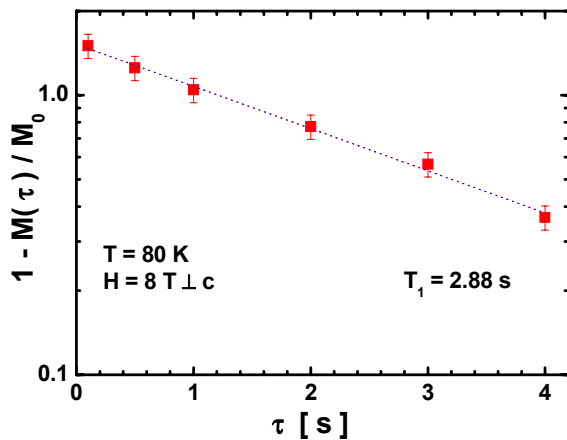

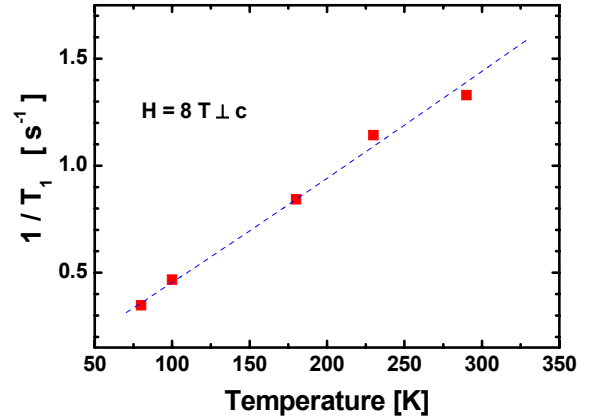Fig. 5. Spin-lattice relaxation recovery of the ^{13}C NMR at 80 K.

Fig. 6. Spin-lattice relaxation rate, $1/T_1$, of the ^{13}C NMR versus temperature.
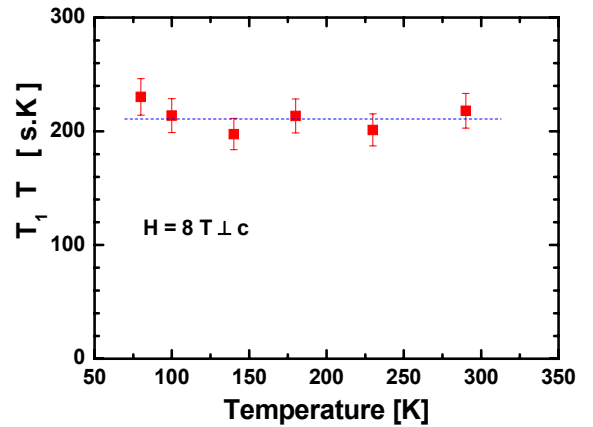

Fig. 7. Temperature dependence of the Korringa product T_1T for the ^{13}C NMR.

In non-magnetic metals, conduction electron is a main relaxation source. Since the spin-flip scattering rate of free carriers is proportional to thermal excitation across the Fermi energy, the relaxation rate $1/T_1$ is proportional to temperature and to the density of states at the Fermi energy; $1/T_1 = 2hk_BT[\gamma_n H_{hf}(i)N(E_F)]^2\beta_i$, where h is the Plank constant, k_B the Boltzmann constant, γ_n the nuclear gyromagnetic ratio, and β_i a numerical factor of order one which differs for the various types of relaxation mechanism i [14]. Consequently, T_1T, which is called the Korringa product, is a constant [15]. Since $1/(T_1T)$ is related to the density of states,

so is K. Thus, this can be combined into one equation; $T_1TK^2 = \xi(\gamma_e/\gamma_n)^2h/(8\pi^2k_B)$, where ξ is a numerical factor and γ_e is the electronic gyromagnetic ratio. This relation is often observed for the most simple *s*-band metals where the spin-lattice relaxation rate and the Knight shift are determined by the Fermi contact interaction. In this equation, the numerical factor ξ is unity for free electrons and reflects the deviation from a free electronic behavior due to many-body and correlation effects [14]. This factor ξ is called the Korringa ratio.

Figure 6 shows a linear increase of $1/T_1$ with temperature. Also, Figure 7 confirms that T_1T is clearly constant for the ^{13}C NMR, indicating that the Korringa relation holds in CaC_6. The T_1T data are averaged to be 210 s·K. Using this value and $K = +0.012\%$, we obtain $\xi = 0.73$, which suggests that the electron spin dynamics in CaC_6 is well described by a nearly free electron picture. This is mainly due to the fact that the itinerant *2s* and *2p* bands dominate without magnetic excitations in CaC_6. The Korringa ratio of $\xi = 0.73$, which is close to unity, suggests that the independent-electron description works quite well in CaC_6, with no complications arising from the many-body effects. For comparison, the Korringa ratios for alkali metals are 1.6 for ^{7}Li and ^{23}Na, 1.3 for ^{39}K, and 1.7 for ^{87}Rb NMR [16]. On the other hand, the spin-lattice relaxation rates of ^{27}Al NMR in magnetic $CeAl_2$ and $GdAl_2$ are extremely high [17] since the *4f* bands for those magnetic systems are partially filled and the spin fluctuation contributes tremendously to the rate.

4. Summary

We have performed ^{13}C NMR measurements to investigate the local electronic structure of a superconducting graphite intercalation compound CaC_6 (T_c = 11.4 K). Many single crystals were stacked and sealed in a quartz tube for naturally abundant ^{13}C NMR. The ^{13}C NMR spectrum shows a single narrow peak with the small Knight shift of +0.012 %, and the small linewidth of ~1.2 kHz. The small value and temperature-independence of both Knight shift and linewidth are typical for non-magnetic metals. The spin-lattice relaxation recovery is single-exponential. The spin-lattice relaxation time T_1 was measured in the normal state as a function of temperature down to 80 K at 8.0 T perpendicular to the c-axis. The $1/T_1$ shows a linear increase as temperature increases, which is called a Korringa behavior and is often observed for typical non-magnetic metals. The relaxation rate and the Knight shift give a Korringa ratio of 0.73, close to unity. This indicates that correlation effects are small and that the independent-electron description works quite well in CaC_6.

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