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Evidence for Strong-Coupling *s*-Wave Superconductivity in MgB_2: ^{11}B NMR Study

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We have investigated a gap structure in a newly discovered superconductor, MgB_2, through measurement of the ^{11}B nuclear spin-lattice relaxation rate, $^{11}(1/T_1)$. $^{11}(1/T_1)$ is proportional to the temperature (T) in the normal state, and decreases exponentially in the superconducting (SC) state, revealing a tiny coherence peak just below T_c. The T dependence of $1/T_1$ in the SC state can be accounted for by an s-wave SC model with a large gap size of $2\Delta/k_BT_c \sim 5$ which suggests it is in a strong-coupling regime.

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Quite recently, Akimitsu and co-workers have discovered a new superconducting (SC) material MgB_2 that reveals a remarkably high SC transition temperature of $T_c \sim 40$ K [1]. MgB_2 crystallizes in the hexagonal AlB_2-type structure, consisting of alternating hexagonal layers of Mg atoms and graphitelike layers of B atoms. The discovery of superconductivity with a relatively high value of T_c in this compound gives a new impact in solid state physics, since it may give other possibilities for finding the high-T_c superconductivity in some binary intermetallic compounds besides cuprates and C_{60}-based compounds. It may be promising to discover new compounds with a high-T_c value exceeding the liquid-N_2 temperature other than cuprates.

Soon after the discovery, Bud'ko and co-workers reported that T_c increases from 39.2 K for $Mg^{11}B_2$ to 40.2 K for $Mg^{10}B_2$, giving a clear indication that electron-phonon interactions are playing an important role [2]. However, the observed high-T_c value of this compound seems to be either beyond or at a limitation for the phonon-mediated superconductivity that was predicted theoretically several decades ago [3]. Therefore, one can speculate that a new exotic mechanism might be possible for the occurrence of the high-T_c superconductivity in MgB_2. In order to gain an insight into a possible mechanism, it is quite important to understand its pairing symmetry and a SC-gap structure.

In this Letter, we report a ^{11}B NMR study that has shed light on the above issues. The nuclear spin-lattice relaxation rate ($1/T_1$) of ^{11}B has been measured in a wide temperature (T) range of 12–280 K. We have found a $T_1T =$ constant behavior in the normal state, and an exponential decrease of $1/T_1$ accompanied with a tiny coherence peak in the SC state. From the T dependence of $1/T_1$ in the SC state that is consistent with an s-wave model with a larger nodeless gap of $2\Delta/k_BT_c \sim 5$ than the BCS value of 3.5, the superconductivity in MgB_2 is concluded to be in a strong-coupling regime and suggested to be mediated by strong electron-phonon interactions.

A polycrystalline sample of MgB_2 was prepared as in Ref. [1]. Electric resistivity and dc magnetization show the SC transition at 39 K as seen in Ref. [1]. Most of the measurements have been performed by using a bulk sample to avoid some crystal defects, if any. T_1 was measured by monitoring the nuclear magnetization after a saturation rf pulse under an external field $H = 13.5$ kOe (18.5 MHz), 29.4 kOe (40.2 MHz), and 44.2 kOe (60.4 MHz). $T_c = 34.5$, 31, and 29 K under $H = 13.5$, 29.4, and 44.2 kOe, respectively was determined by ac-susceptibility measurements using an *in situ* NMR coil, as shown in the inset of Fig. 1. These results are in good agreement with those reported recently [4,5]. The onset temperatures of the SC state are also corroborated by the broadening in the ^{11}B NMR spectrum, associated with the field distribution in the SC mixed state. In the low field of $H = 13.5$ kOe where the ^{11}B NMR intensity below $T_c(H)$ is remarkably reduced because of the diamagnetic shielding of the rf pulse, we used the powdered sample that was moderately crushed into a large size of grains. The Knight shift of ^{11}B in MgB_2 was determined with respect to the resonance frequency of $B(OH)_3$ ($K[B(OH)_3] \sim 20$ ppm).

We have observed a typical electric-quadrupole broadened ^{11}B NMR spectrum for the polycrystal MgB_2 from which an electric-field frequency of $\nu_Q \sim 0.833$ MHz was estimated. This result is in good agreement with those reported recently [6,7]. The linewidth of the central peak in the ^{11}B NMR spectrum (the $1/2 \leftrightarrow -1/2$ transition) is as small as $\sim$15 kHz, showing good quality of the sample. Its resonance shift, i.e., the Knight shift (^{11}K), does not show any T dependence in the normal state, revealing a very small value of $K(MgB_2) \sim 70$ ppm [8]. Although ^{11}K decreases slightly below T_c, the large SC diamagnetic contribution as well as the very small Knight shift prevent us from measuring the variation of the spin susceptibility across T_c at the present.

The T_1 measured at the central peak was determined by fitting the relaxation function of the nuclear magnetization $m(t)$ to the following theoretical two-exponential form [9]:

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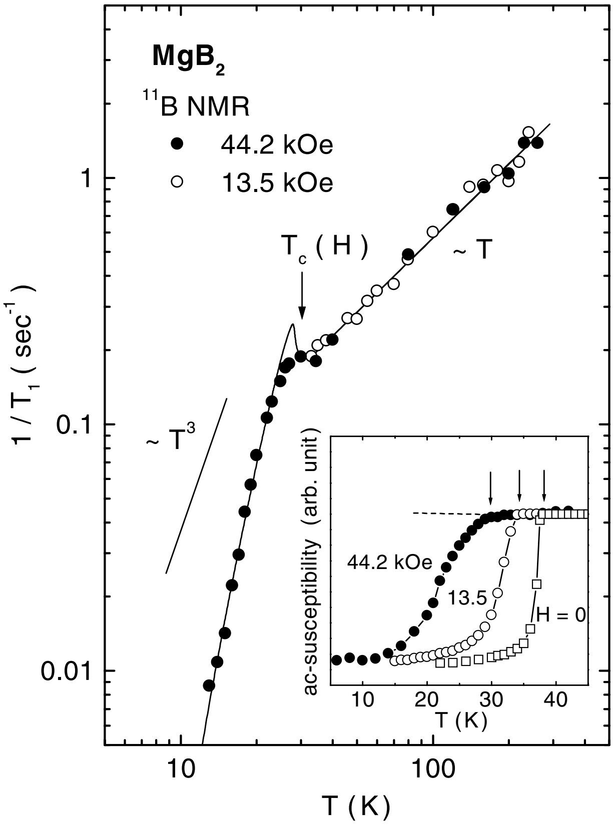

FIG. 1. T dependence of $^{11}(1/T_1)$ in a bulk sample of MgB$_2$. Closed and open circles correspond to $1/T_1$ at the external field $H = 44.2$ and 13.5 kOe, respectively. Solid curve in the SC state is the calculation on the base of a conventional s-wave model (see text) [13]. The inset displays the T dependence of ac susceptibility for the powdered sample at $H = 0$ and 13.5 kOe (open squares and circles) and for the bulk sample at $H =$ 44.2 kOe (closed circles). The measurements were performed by using an *in situ* NMR coil. The respective arrows show the onset temperature of superconductivity at $H = 0$, 13.5, and 44.2 kOe.

$$m(t) = \frac{M(\infty) - M(t)}{M(\infty)} = \frac{1}{10}\exp\left(-\frac{t}{T_1}\right) + \frac{9}{10}\exp\left(-\frac{6t}{T_1}\right). \quad (1)$$

Here, $M(t)$ is the nuclear magnetization at a time t after saturation pulses. From good fits to this formula, a single component of T_1 was precisely determined over a measured T range, although a short component of T_1 appears at low temperatures, associated with the presence of vortex cores in the SC mixed state. The relaxation component ascribed to the vortex core in the mixed state will be discussed in a separated paper.

Figure 1 shows T dependence of $1/T_1$ on the bulk sample, where $1/T_1$ in both the normal and the SC states at $H = 44.2$ kOe and only in the normal state at $H =$ 13.5 kOe are plotted. In the normal state, $1/T_1$ is independent of the field, following a $T_1T =$ constant relation with $T_1T = 1.8 \times 10^2$ s K down to T_c. If we assume that some orbital contribution to ^{11}K is negligibly small, the experimentally derived Korringa relation of $1/T_1T\ K^2 \sim 11.3 \times 10^5\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$ is 2.9 times larger than a calculated value of $1/T_1T\ K^2 = (4\pi k_B/\hbar)(\gamma_n/\gamma_e)^2$ of the ^{11}B nucleus.

Next we discuss the behavior of $1/T_1$ in the SC state to examine the pairing symmetry and the SC gap structure. In general, R_s/R_n [$\equiv (1/T_{1s})/(1/T_{1n})$] is related to the density of states (DOS) in the SC state, where $1/T_{1s}$ $(1/T_{1n})$ corresponds to the data in the SC (normal) state.

We have found a tiny coherence peak in R_s/R_n just below T_c that was observed irrespective of the value of magnetic fields as seen in Fig. 2 [10]. The coherent peak is clear when the R_s/R_n in the SC state is plotted in a linear scale as shown in Fig. 3 and is compared with the ac susceptibility result showing an onset of the SC transition. It is obvious that R_s/R_n shows a tiny peak just below T_c, followed by a marked decrease below $\sim 0.8T_c$. These behaviors are quite in contrast with R_s/R_n in unconventional superconductors with a line-node gap such as high-T_c cuprate and heavy-fermion compounds. A typical example of the monotonous decrease below T_c was observed in Sr$_2$RuO$_4$ with a line-node gap, as shown in Fig. 3 for comparison [11].

It is well known that the T variation of R_s/R_n in the SC state is related with the SC gap structure. Figure 4 shows an Arrhenius plot of $T_c(H)/T$ vs R_n/R_s, where $T_c(H)$ is the SC transition temperature under the magnetic field. In this plot, an exponential T dependence corresponds to a linear relation. R_n/R_s under the various magnetic fields

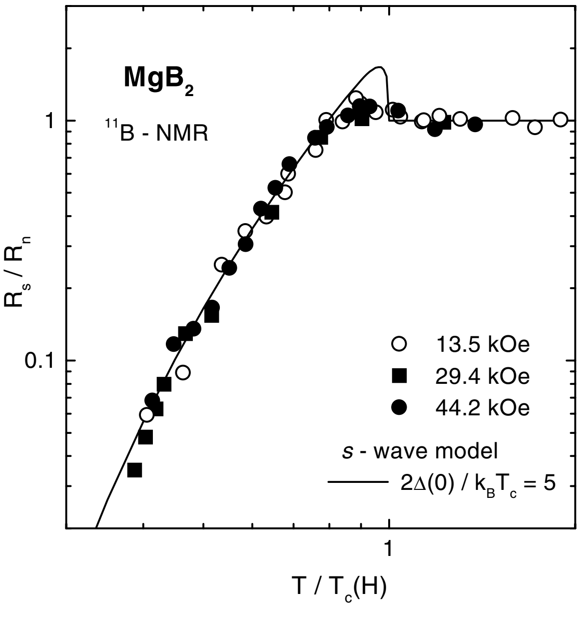

FIG. 2. R_s/R_n is plotted against $T/T_c(H)$ where T_c (13.5 kOe), T_c (29.4 kOe), and T_c (44.2 kOe) are 34.5, 31, and 29 K, respectively. The solid curve shows the calculation on the basis of the s-wave model with $2\Delta_0/k_BT_c = 5$ (see text).

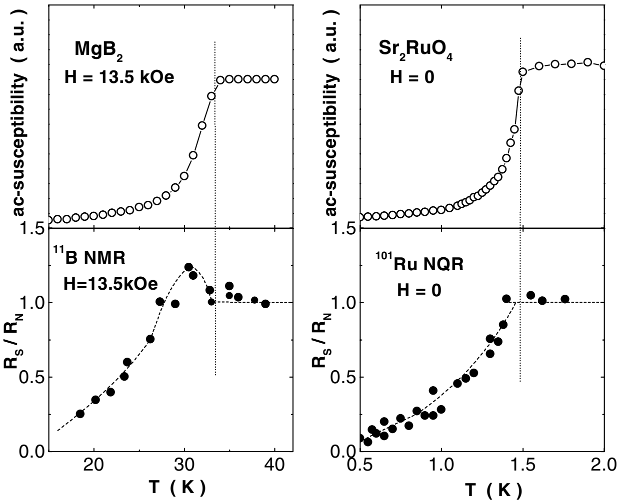

FIG. 3. T dependence of ac susceptibility and $R_s/R_n \equiv (1/T1)_s/(1/T_1)_n$ in MgB$_2$ and Sr$_2$RuO$_4$ [11].

reveals almost the same dependence on $T_c(H)/T$, reflecting an intrinsic behavior associated with the SC gap structure. Evidently, R_n/R_s obeys the exponential dependence down to $0.39T_c(H)$. This behavior is inconsistent with a T^4 dependence that is expected for a point-node gap. The magnitude of the SC gap could be rather estimated from a coefficient of the linear relation as $2\Delta/k_BT_c \sim 5$, that is 1.4 times larger than the BCS value of 3.5. The T dependence of R_n/R_s in the SC state reveals that the SC gap possesses a finite-gap structure.

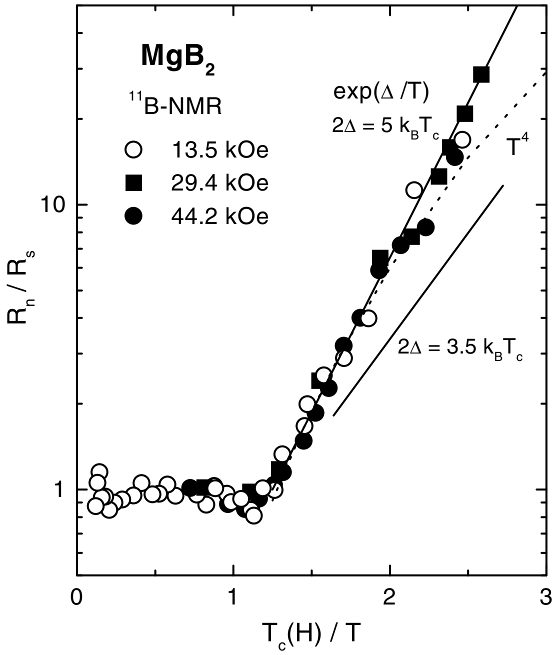

FIG. 4. Arrhenius plot of R_n/R_s vs $T_c(H)/T$. A linear line shows an exponential dependence.

Next, the result is quantitatively compared with theoretical models. R_s/R_n is expressed using the SC DOS, $N_s(E)$ as follows:

$$\frac{R_s}{R_n} \propto \frac{2}{k_BT}\int_0^\infty [N_s(E)^2 + M(E)^2]f(E)[1 - f(E)]\,dE\,, \tag{2}$$

where $M(E)$ and $f(E)$ are the so-called *anomalous* DOS arising from the coherence effect of scattering inherent to a spin-singlet SC state and the Fermi-distribution function, respectively [12]. Note $M(E) = 0$ in the case of unconventional superconductors such as p- or d-wave symmetries. When the SC gap possesses line nodes or point nodes, R_s/R_n shows T^2 and T^4 dependences (which correspond to $1/T_1 \sim T^3$ and T^5, respectively), whereas the finite gap results in an exponential dependence in R_s/R_n. The experimental result of R_s/R_n that reveals a tiny coherence peak followed by an exponential decrease strongly suggests the s-wave state with a finite gap. Actually, the T dependence of R_s/R_n, except just below T_c, can be well reproduced by a calculation based on a typical s-wave model as shown in Figs. 1 and 2, in which a phenomenological energy broadening function in $N_s(E)$ is assumed to be of a rectangle type with a width 2δ and a height $1/2\delta$ as presented by Hebel [13]. The SC-gap sizes of $2\Delta/k_{\mathrm{B}}T_{\mathrm{c}} \sim 5$ and $\delta/\Delta(0) \sim 1/3$ are adopted in the calculation. The salient findings of the tiny coherence peak in R_s/R_n just below T_c and its exponential decrease below $0.8T_c$ provide convincing evidence for the spin-singlet s-wave pairing realized in MgB$_2$. The SC-gap value larger than the weak-coupling BCS one suggests that the superconductivity in MgB$_2$ is in a strong-coupling regime.

It should be noted that the coherence peak is largely suppressed compared with that expected for the ordinary s-wave model. As for the origin of the suppression, the following effects can be considered: (i) some large wave-number dependence of the SC energy gap, that points to an anisotropic s-wave, and (ii) some intense quasiparticle broadening just below T_c due to interaction with thermally excited phonons. In the former, the anisotropic SC gap may originate from an anisotropy of the Fermi surface and/or of a pairing interaction, and it may be possible to observe the larger coherence peak in $(1/T_1T)$ when nonmagnetic impurities are doped. This is because the doped impurities average over the anisotropy of the energy gap and, as a result, the renormalized gap due to the impurity scattering becomes more isotropic or even larger than in the undoped compound [14]. However, our preliminary result on $1/T_1$ in the Al-doped MgB$_2$ shows that the coherence peak is insensitive to the Al concentration, suggesting that the former might not be the main effect. Rather, the latter is dominant since the strong electron-phonon coupling may give rise to the large lifetime broadening of quasiparticles just below T_c by thermally excited phonons. In fact, the T dependence of $1/T_1T$ in the SC state of MgB$_2$ is quite similar to that in the Chevrel-phase compound

$TlMo_6Se_{7.5}$ with $T_c = 12.2$ K and $2\Delta/k_BT_c \sim 4.5$ [15], in which the coherence peak is remarkably suppressed as well. In addition, similar suppression of the coherence peak just below T_c ($R_s/R_n \sim 1.2$) was also reported in Rb_2CsC_{60} with relatively higher $T_c \sim 31$ K, although it is even in a weak-coupling regime [16]. It can be considered that the large suppression of the coherence peak is inherent to s-wave superconductors with higher T_c.

The present result of $1/T_1$ in the whole T range of MgB_2 differs from that of cuprates such as $La_{1.85}$-$Sr_{0.15}CuO_4$ with a comparable T_c value of 38 K [17,18]. The $1/T_1T$ in the cuprates shows a Curie-Weiss behavior in the normal state, evidencing that the superconductivity appears on the verge of antiferromagnetism. The $1/T_1$ in the SC state decreases sharply without the coherence peak just below T_c, followed by a T^3 dependence far below T_c. This evidences that the symmetry of the Cooper pairs is of a d-wave type with a line-node gap. Various experiments reported thus far tell us that the Cooper pairs are presumably mediated via magnetic interactions other than electron-phonon interactions. On the other hand, the T dependence of $1/T_1$ in MgB_2 shows that magnetic correlations are absent in the normal state and that the SC state is characterized by the large nodeless gap that is consistent with the strong-coupling s-wave superconductor. In this context, it is natural to consider that the mechanism of the superconductivity in MgB_2 is quite different from in the cuprates. Rather the electron-phonon interactions may play an important role. We suggest that the high value of T_c in MgB_2 may be due to the strong electron-phonon coupling via some phonon modes inherent to the presence of layers including light-element boron atoms.

In conclusion, we have reported that the $1/T_1$ of ^{11}B decreases exponentially in the SC state, revealing a tiny coherence peak just below T_c. The T dependence of $1/T_1$ in the SC state can be accounted for by a spin-singlet s-wave model where $2\Delta/k_BT_c \sim 5$ is substantially larger than the weak-coupling BCS value of 3.5. It is suggested that the strong electron-phonon interactions may play an important role for the high-temperature superconductivity in MgB_2.

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