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Superconducting energy gap and antiferromagnetic spin fluctuations in the superconductor YNi_2B_2C: An NMR study

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Pulsed NMR studies of ^{11}B and ^{89}Y have been carried out in the recently discovered quaternary borocarbide superconductor YNi_2B_2C ($T_c = 15.5$ K). These results are as follows: (a) *Superconducting state:* Though there is only one crystallographic B site in this structure, we have observed two ^{11}B resonances in the superconducting state. One signal comes from a superconducting region, and the other from a normal-metal region. As for the former signal, the nuclear relaxation rate, T_1^{-1} decreases drastically with further decrease of temperature with no appreciable enhancement just below T_c, and it starts to saturate below 6 K. (b) *Normal state:* $(T_1T)^{-1}$ increases as temperature decreases. We interpret this temperature dependence as arising due to two-dimensional or three-dimensional antiferromagnetic spin fluctuations (structure of YNi_2B_2C is tetragonal and highly anisotropic).

Discovery of superconductivity[1,2] in Y-Ni-B-C laid down the foundation of a new area of research in superconductivity, namely, the field of quaternary rare-earth transition-metal superconducting and magnetic borocarbide, RM_2B_2C (R rare-earth metal, M transition metal). Subsequently, superconductivity was reported in a multiphase quaternary system Y-Pd-B-C (in which Ni was replaced by Pd) at a rather high superconducting transition temperature, $T_c \sim 23$ K, in the composition $YPd_5B_3C_x$ (Ref. 3) and $T_c \sim 22$ K in $YPd_4BC_{0.2}$.[4] This is the highest T_c reported in any bulk intermetallic superconductor. Several other materials RNi_2B_2C were also reported to be superconducting with T_c ranging between 8 K and 16.5 K.[5,6] Following the structure of $LuNi_2B_2C$ ($T_c = 16.5$ K) determined by Siegrist *et al.*,[7] the presence of alternating YC and Ni_2B_2 layers in the anisotropic tetragonal structure of YNi_2B_2C raises the possibility that these quaternary borocarbides may be a series of quasi-two-dimensional (2D) high-T_c superconducting compounds analogous to the cuprates. Since the density of states peak in $LuNi_2B_2C$ exists near the top of nearly filled Ni $3d$ bands,[8] the $3d$ electronic correlation of Ni in the Ni_2B_2 layer of RNi_2B_2C is of great importance. In order to study the nature of the electronic correlation and to get a better understanding of the superconductivity in YNi_2B_2C and a basic difference between RM_2B_2C and RRh_4B_4 superconductors from a microscopic point of view, we have performed ^{11}B and ^{89}Y NMR measurements. We present here the results of these studies.

YNi_2B_2C was prepared by melting high-purity elements of Y (99.9%), Ni (99.9%), B (99.8%), and C (99.7%) in an arc furnace under argon gas. The ingot was turned and melted several times to ensure homogeneity. The sample was then annealed at 1050 °C for 30 days. X-ray-diffraction measurements showed the formation of the sample in a $ThCr_2Si_2$ structure with lattice parameters in agreement with the published data.[5] Traces of impurity phases YB_2C_2 and Ni_3C could be seen in the x-ray patterns. Phase purity of the sample improved upon annealing. T_c of the sample, as determined from ac susceptibility measurements, is 15.5 K. ^{11}B and ^{89}Y NMR measurements were carried out using conventional pulse techniques in applied magnetic fields of 1.4 T and 4.3 T, respectively. The Knight shift of ^{11}B, ^{11}K, was determined with respect to the resonance of ^{11}B in $(OCH_3)_3B$ in an applied field of 3.3 T. Magnetic susceptibility, χ, measurements were performed by a torsion-type magnetic balance method.

Figure 1 shows the ^{11}B NMR spectra for the well-aligned powder in a favorable direction, which is perpendicular to the c axis, with magnetic field. Since B atoms in YNi_2B_2C have a uniaxial local symmetry, the electric quadrupole (eqQ) interaction with an axially symmetric electric field gradient of B ($I = 3/2$) is fully expected. The quadrupole frequency, ν_Q, is estimated to be ~ 0.69 MHz from the separation between the resonance frequency for the two satellite lines. These spectra have been taken at a constant frequency of 19 MHz by sweeping an external field of ~ 1.4 T (T_c of the sample is reduced to ~ 12 K in this field). While the central line is quite narrow in the normal state, the two components are clearly seen below T_c. One of the signals shifts to higher magnetic field, and the other signal does not shift

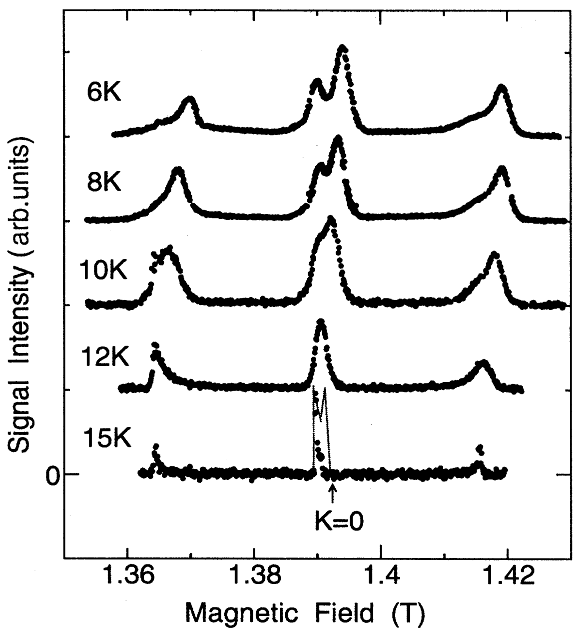

FIG. 1. ^{11}B spin-echo NMR spectra of YNi_2B_2C for a well-aligned powder by magnetic field. The dotted line at 15 K shows an expected NMR pattern for a randomly oriented powder with the second-order *eqQ* interaction.

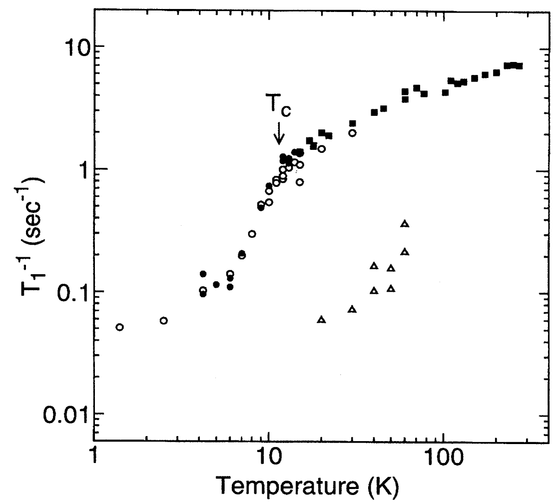

FIG. 2. Temperature dependence of the nuclear spin-lattice relaxation rate, T_1^{-1} of ^{11}B and ^{89}Y in YNi_2B_2C. Solid and open circles correspond to the central and satellite shifted B signals in the superconducting state, respectively. Closed squares and open triangles show T_1^{-1} of ^{11}B and ^{89}Y in the normal state, respectively.

so much through T_c. The former and the latter correspond to the signals belonging to the superconducting and nonsuperconducting (normal-metal) regions, respectively, which will be mentioned later. The intensity of this signal is quite significant compared with that of the "superconducting region" signal, which implies that a substantial fraction of the sample is nonsuperconducting. It should also be pointed out that the satellite lines corresponding to the unshifted central line are not so well defined, though they are discernible as very broad humps at lower fields. This is suggestive of a distribution of the quadrupole interaction energy in the spectrum corresponding to a "normal-metal region" signal. That the nonsuperconducting (normal-metal) fraction of the sample is an impurity phase can easily be ruled out, considering that the strength of the unshifted NMR signal is quite significant and the powder x-ray diffraction pattern does not indicate any impurity phase of this extent (impurity lines do not have intensity higher than 5% of the main line). One possible explanation of the "normal-metal region" signal observed below T_c is the following: The "normal-metal region" signal arises from those regions of the sample wherein the occupancy of B and/or C sites varies, at a microscopic level, from the ideal one. For example, there could be an interchange of B and C and/or there could be vacancies at these sites. Such finer structural aspects cannot be resolved by x-ray diffraction, because they do not give rise to new diffraction lines and also because the scattering factors of B and C are rather small. Only with a microscopic technique such as NMR can such details be seen. A very similar situation has already occurred in the single-phase sample of $YBa_2Cu_3O_{7-z}$,[9] for instance. This similarity becomes quite striking if we express the stoichiometry of the sample as $YNi_2B_{2-x}C_{1-y}$ where x and y define B and C deficiency. Regions consisting of the "defect" unit cell and the cells surrounding it are rendered nonsuperconducting. Clearly, the nonsuperconducting fraction of the sample depends on the stoichiometry of the sample and its annealing history. Besides the present work, there are two other reports on NMR measurements of YNi_2B_2C below T_c. In one of them,[10] an annealed sample was used, just as in the present studies, and two ^{11}B resonances were observed. In the other work[11] using an unannealed one, the authors do not report having seen a "normal-metal region" signal below T_c. In the unannealed sample, the resonance lines corresponding to the superconducting and nonsuperconducting regions may be somewhat broader and, therefore, may not be resolved. As mentioned earlier, this has also emphasized the importance of annealing the material. NMR studies, therefore, are of great importance in studying the composition-property relationship in borocarbides and provide an effective characterization tool to study it.

Next, in the intermediate magnetic field, H, $H_{c1}<H<H_{c2}$ for a type-II superconductor, vortices generally form a dense (typically triangle) lattice. Here H_{c1} and H_{c2} are the lower and upper critical fields, respectively. The distance between the nearest-neighbor filaments (vortices), d, can be estimated to be ~ 410 Å for an applied magnetic field of ~ 1.4 T. The inhomogeneous width of the local field, ΔH, is given from the second moment by using penetration depth λ (Ref. 12) and d. Thus we obtain ΔH to be ~ 70 Oe. Owing to the superposition of the nearest-neighbor contribution, ΔH of the order of H_{c1} is usually considered to be comparable to the negative shift, δH, of the spectrum associated with demagnetization of type-II superconductors under an external field.[13] So we can estimate the values of ΔH or δH as 50 Oe, which agree with the measured values of 40–80 Oe. Accordingly, the negative shift and excess line broadening of the NMR signal are qualitatively explained by magnetic-field inhomogeneity and demagnetization in the mixed state of type-II superconductors.

Shown in Fig. 2 is the temperature dependences of the spin-lattice relaxation rate, T_1^{-1} of ^{11}B and ^{89}Y measured in a wide temperature range. From a rather narrow B signal in the normal state, T_1 of ^{11}B ($I=3/2$) was obtained by monitoring the recovery of nuclear magnetization after a single $\pi/2$ rf pulse in the central line. If the excitation between nuclear spin levels could be achieved with a weak rf pulse as to saturate only $\pm 1/2$ levels, the data were fitted to the following recovery equation:

$$\frac{M(\infty)-M(t)}{M(\infty)}=0.1\exp(-2Wt)+0.9\exp(-12Wt),$$

hereafter referred to RI, where t and $2W(=T_1)$ are the variable delay time after a $\pi/2$ pulse and transition probability, respectively. Now, in the superconducting state, if there exists a difference in ν_Q between superconducting and normal-metal regions, we might clearly measure T_1 of B in a superconducting region from the shifted satellite. T_1 can be determined by using the following recovery equation:

$$\frac{M(\infty)-M(t)}{M(\infty)}=0.1\exp(-2Wt)+0.5\exp(-6Wt)+0.4\exp(-12Wt),$$

referred to RII. As seen in this figure, T_1 values measured from the central line by RI between 12 K and 30 K are in agreement with those from the satellite line by RII, and T_1's for both the shifted central and satellite lines are not different so much in the superconducting state as a result. As is well known, the largest nuclear relaxation component is dominant in the mixed nuclear relaxation rates. Estimating from the "normal-metal region" relaxation rates measured below 6 K, T_1 from the unshifted signal may be eight to ten times longer than that from the superconducting region. This is consistent with that the recovery data from the shifted signal were fitted very well by only RI or RII till the value of the righthand side in the recovery equation became 0.03–0.05 in total relaxation data. Thus, while there exists the central line with barely resolved satellite line, the measured relaxation may come mainly from the "superconducting region" signal. Consequently, the temperature dependence of these relaxation rates in the superconducting state has the following features: With further decrease of temperature, T_1^{-1}'s of the shifted central and satellite signals (indicated by solid and open circles, respectively) decrease drastically with no appreciable enhancement just below T_c, and start to saturate below 6 K. The behavior is considered to be due to the appearance of the relaxation rate from the normal region, which becomes relatively larger than that from the superconducting one below 6 K.

Then, the measured T_1^{-1} of ^{89}Y in external field of 4.3 T are also indicated by open triangles in Fig. 2. As can be seen in the B spectrum, the observed half width of 20 Oe in the Y spectrum may contain excess width due to presence of the "normal-metal region." The tentatively estimated value T_1T of Y at 20 K is ~330 s K, which is much larger as compared with the value of 92 s K for YRh_4B_4.[14] This result suggests that the Y density of states at the Fermi energy for

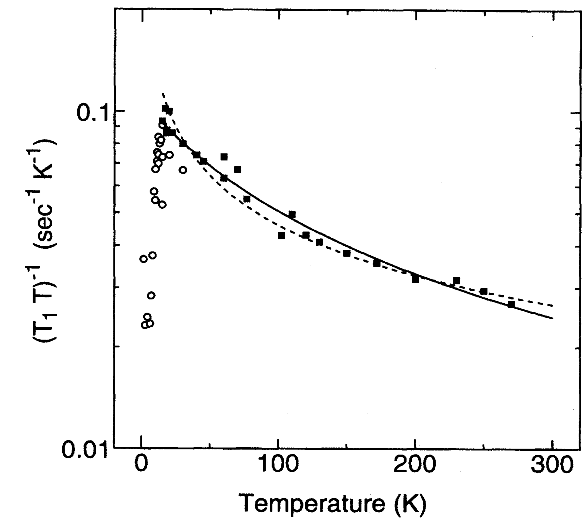

FIG. 3. Analysis of the temperature dependence of $(T_1T)^{-1}$ for ^{11}B. Solid squares and open circles are the measured values of relaxation in the normal and superconducting states, respectively. The solid and dotted lines show the calculated values by SCR theory, which correspond to $(T_1T)^{-1}=9.86/(T+98.1)$ and $(T_1T)^{-1}=0.465/(T+0.0273)^{1/2}$ for 2D AF and 3D AF, respectively (see text).

YNi_2B_2C is very low, although the difference in the atomic hyperfine field in the two compounds should also be appropriately considered.

Next, let us consider the temperature dependence of the relaxation rates in the normal state. As is well known, according to the self-consistent renormalization (SCR) theory for itinerant antiferromagnetic (AF) spin fluctuations developed by Moriya *et al.*,[15] T_1^{-1}'s are proportional to $T/(T-T_N)$ and $T/(T-T_N)^{1/2}$ for 2D and 3D itinerant anti-

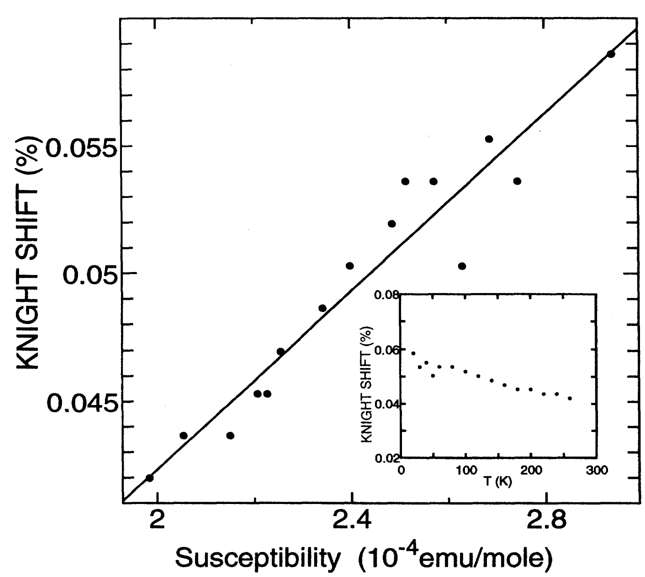

FIG. 4. ^{11}K is plotted against χ with temperature as an implicit parameter. Inset: ^{11}K versus T.

ferromagnets, respectively, when the staggered spin susceptibility above T_N obeys the Curie-Weiss law. Here T_N is the Néel temperature.

Figure 3 shows the temperature dependence of $(T_1T)^{-1}$ for B. The best fitness to the measured relaxation rates (indicated by open circles and closed squares) in 2D and 3D AF is obtained as $(T_1T)^{-1}=9.86/(T+98.1)$ and $(T_1T)^{-1}=0.465/(T+0.0273)^{1/2}$ for 2D (indicated by solid line) and 3D AF (indicated by dotted line), respectively. These results suggest that the fitted curves for both the 2D and 3D AF cases were in agreement with the measured values. Accordingly, we can regard YNi_2B_2C as itinerant AF spin fluctuating material, in which $3d$ electronic correlation plays a significant role.

Now, the temperature dependence of the Knight shift of ^{11}B, ^{11}K, was measured at the peak position of the B spectrum for an oriented powder in a field of 3.3 T, which is shown in the inset of Fig. 4. From the slope of ^{11}K versus χ plot with temperature as an implicit parameter shown in Fig. 4, the hyperfine coupling constant, $^{11}A_{\rm hf}$ of ^{11}B was determined to be $+9.75$ kOe/μ_B, which is much larger than the expected value. Quantitative evaluation for $^{11}A_{\rm hf}$ including anisotropy will be performed in the near future.

Incidentally, the ratio $2\Delta/k_BT_c$, where Δ is the value of the superconducting gap, as measured in the tunneling experiments,[16] lies in the range 3.7–4.5. Similarly, the normalized specific-heat jump $\Delta C/\gamma T_c$ at T_c has been reported to be 1.77 (Ref. 17), 2.6 (Ref. 18), and ~3 (Ref. 6), which are larger than the BCS value (=1.43). Thus it is clear that in view of the diversity of these results, more work is required to settle the issue of whether YNi_2B_2C is a weakly coupled or strongly coupled superconductor.

In summary, we observe two ^{11}B NMR signals below T_c in the recently discovered superconductor, YNi_2B_2C, one belonging to the superconducting region and the other belonging to the normal-metal region. The measured T_1^{-1} corresponding to the former signal drastically decreases with no appreciable enhancement just below T_c. The relaxation measurements of ^{11}B in the normal state suggest that antiferromagnetic spin fluctuations play an important role. This implies that Ni atoms carry moments (there are no other moment-bearing atoms in a unit cell), at least at the NMR time scale.

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