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NMR investigation of the quaternary-intermetallic-compound superconductor YNi_2B_2C

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Measurements of the ^{11}B NMR spectrum, isotropic Knight shift (K_i), and spin-lattice relaxation rate ($1/T_1$) in an unoriented powder sample of YNi_2B_2C are reported in the normal and the superconducting states. In the normal state, K_i varies linearly from $(+5.7\pm0.7)\times10^{-4}$ at 300 K to $(+4.9\pm0.7)\times10^{-4}$ just above the superconducting transition temperature. The anisotropic Knight shift, if present, is substantially smaller than K_i. An anomalous increase in $(T_1T)^{-1}$ with decreasing temperature (T) is found in the normal state. From the behavior of the NMR linewidth in the superconducting state, the low-temperature limit $\lambda(0)=(108\pm5)$ nm is found for the penetration depth. At the superconducting transition, $1/T_1$ drops rapidly and no Hebel-Slichter peak is seen.

I. INTRODUCTION

Recent reports of electrical transport properties,[1,2] magnetic properties,[1–4] and the crystal structure[5] of compounds with the formula RNi_2B_2C (R=Y,Tm,Er,Ho,Lu) have caused a lot of interest in this class of quaternary intermetallic compounds because they are true quaternary superconductors, they have moderately high superconducting transition temperatures (T_c),[1,2] and magnetism and superconductivity coexist in some of them.[2,4] Two of the interesting features of one member of the series, $LuNi_2B_2C$,[6] are that there is a relatively sharp structure in the calculated density of states very close to the Fermi energy and that all four components of the compound contribute significantly to the density of states at the Fermi energy.

In this paper we present a preliminary report of the NMR properties of ^{11}B in YNi_2B_2C in the normal and the superconducting states. The primary motivation for this work is to study the microscopic electronic and the superconducting properties of this quaternary superconductor.

II. SAMPLE

The sample of YNi_2B_2C used in this study was prepared by arc-melting. The starting materials were Y metal shavings (99.99%), Ni metal shavings (99.998%), a coarse boron chunk (99.9995%), and graphite. The 0.140 mg sample was arc-melted under Ar on a standard water-cooled copper hearth twice. Overall loss in weight in the entire melting process was about 1.5%. No annealing after the arc-melting was necessary to obtain the superconducting phase.

The superconducting response of the polycrystalline material was characterized by a low-field dc magnetization measurement using a commercial superconducting quantum interference device magnetometer over the temperature (T) range 5–20 K. Zero-field cooling followed by application of a 1 Oe magnetic field yielded perfect diamagnetism when a demagnetization factor of 0.54 was used for the ellipsoidal-shaped sample. Field cooling showed a Meissner effect that is 3% of the value for perfect diamagnetism, which indicates that the superconductivity is a bulk effect. Our NMR measurements show that at most a few percent of the sample is not superconducting. The onset of superconductivity obtained from the shielding curve occurs at 15.5 K with an inductive transition width of 1.3 K. The transition temperature was also confirmed by resistivity measurements. Although an x-ray analysis has not been done on this sample, other ones prepared by the same steps have an x-ray pattern that indicates less than 5% of other phases are present. This chunk was then ground into a coarse powder for NMR measurements, whose spectrum (discussed below) indicated a high quality, single phase.

III. EXPERIMENTAL DETAILS, RESULTS, AND PARAMETERS

All of the NMR measurements were made with a laboratory-built pulsed NMR spectrometer. The free induction decay (FID) or spin-echo signals were captured and averaged on a digital oscilloscope, after which they were transferred to a personal computer for storage and analysis. Cryogenic temperatures were provided by a laboratory-built helium gas flow cryostat with electronic temperature regulation.

The properties of the ^{11}B nucleus used in this work are[7] nuclear spin $I=\frac{3}{2}$, gyromagnetic ratio $\gamma/2\pi=13.656(1)$ MHz/T, electric quadrupole moment $Q=3.6\times10^{-24}$ cm^2, and a natural abundance of 80.4%. Since the full width of the first-order quadrupolar powder pattern NMR spectrum was found to be about .05 T, we chose to saturate the full linewidth to separate spin-lattice relaxation from recovery of the magnetization via spectral diffusion to a hole burned in the

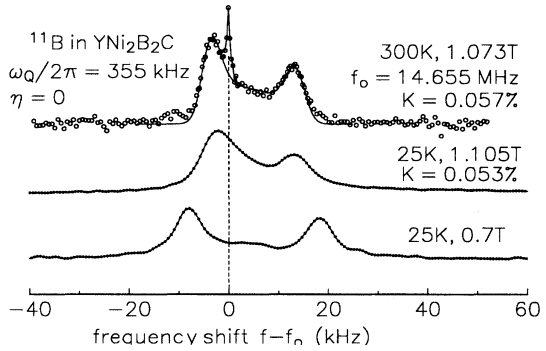

FIG. 1. ^{11}B NMR central $(-\frac{1}{2}\leftrightarrow+\frac{1}{2})$ transition absorption spectra of powdered YNi_2B_2C at different temperatures and applied fields. The narrow peak in (a) is a liquid marker (carboranyl methyl propionate) with zero-field shift and the solid line is a fit to the spectra using $K_i=0.057\%$, $K_a=0$, $\eta=0$, and $\omega_Q/2\pi=355$ kHz.

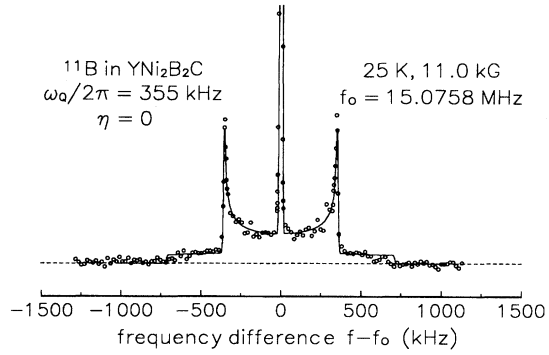

FIG. 2. ^{11}B NMR satellite transition absorption spectra of powdered YNi_2B_2C. The solid line is a fit to the data using the same parameters as for Fig. 1.

inhomogeneously broadened NMR line and to avoid the multiple exponential recovery that occurs when different transitions in a quadrupolar split line recover from different initial spin temperatures. Nearly complete destruction of the initial magnetization for the entire line was obtained by using a saturating pulse train whose frequency was swept across the entire spectrum and then using a spin-echo or FID signal at resonance to measure the recovery of the magnetization. This procedure yielded a single exponential recovery and a typical uncertainty of $\lesssim 5\%$ for the spin-lattice relaxation rate $(1/T_1)$. A substantially lower degree of initial magnetization destruction always led to a faster recovery that deviated significantly from a single exponential.

According to the reported structure of YNi_2B_2C,[5] all of the boron sites are crystallographically equivalent and have a local symmetry that generates an axially symmetric electric field gradient. The corresponding quadrupolar powder pattern NMR spectrum has, therefore, a distribution of second-order splittings of the central transition $(-\frac{1}{2}\leftrightarrow\frac{1}{2})$ and a distribution of first-order splittings of the satellite transitions $(-\frac{3}{2}\leftrightarrow-\frac{1}{2}$ and $\frac{1}{2}\leftrightarrow\frac{3}{2})$.[8] In Fig. 1, several central transition spectra obtained from the Fourier transform of the FID are shown that include two values of the applied magnetic field (B_0). The narrow peak in Fig. 1(a) at 300 K is the signal from a liquid marker (carboranyl methyl propionate) whose ± 20 ppm shift is negligible in the context of the present measurements. Field shifts at lower values of T were obtained by holding the external field constant. The solid line is a fit to the data using the parameters (isotropic Knight shift) $K_i=5.7\times10^{-4}$ (anisotropic Knight shift) $K_a=0$ (electric field gradient asymmetry parameter) $\eta=0$ (quadrupolar interaction frequency) $\omega_Q/2\pi=(1/8\pi)e^2qQ=(355\pm10)$ kHz (notation of Ref. 9), and a nuclear dipolar broadening rms width of 1.6 G. This value for the dipolar width is calculated on the basis of the volume density of ^{11}B in the sample. Figure 2 shows the first-order powder pattern of the satellite transitions that were recorded using frequency-shifted and summed (FSS) Fourier transform processing.[9] The solid line is a fit[10] to this spectrum using the same Knight shift and quadrupolar parameters as in Fig. 1. Both fits also agree with the theoretical satellite-central transition intensity ratio of 3:4. The splitting of the peaks of the central transition at 25 K [Figs. 1(b) and 1(c)] is inversely proportional to B_0 as expected of the second-order quadrupolar transition. At the lower T, there is also some additional broadening of the NMR absorption line in comparison to the spectrum at 300 K whose origin is not understood and K_i has decreased slightly to $(5.3\pm0.7)\times10^{-4}$ at 25 K.

The close fit of the parameters to the measured spectra for different magnetic fields and spectral features is a strong argument that our assignment is correct. The absence of a different quadrupolar spectrum or Knight shift from other phases indicates that nearly all of the sample is the same phase.

Other properties of the NMR spectrum not shown in detail here are (1) an approximately linear decrease in K_i from $(+5.7\pm0.7)\times10^{-4}$ at 300 K to $(+4.9\pm0.7)\times10^{-4}$ just above the superconducting transition temperature (10.5 K at 1 T), (2) a sharp increase in the width of the central transition with decreasing T in the superconducting state with a square root second moment $\Delta B=(80\pm7)$ G at 1.5 K $(T/T_c=0.14)$ that we attribute to the field distribution of the vortex structure, and (3) the fractional field shift of the centroid of the central transition is changed to the substantially lower value -0.3% at $T/T_c=0.3$. This latter shift is the sum of the diamagnetic contribution of the volume magnetization of the sample in the superconducting state and the Knight shift. The analysis at the end of the next section shows that within its uncertainty, all of this shift can be accounted for by the sample magnetization. Thus, it is not possible to obtain the much smaller K_i in the superconducting state from these experiments.

Measurements of the ^{11}B spin-lattice relaxation rate $1/T_1$ are shown in Fig. 3, where $1/T_1T$ is plotted as a function of T over the range 1.5 K$<T<$300 K at $B_0=1.105$ T. At this value of B_0, the reported value of T_c (Ref. 3) is 10.2(5) K, which agrees with the value we infer from the peak in $1/T_1$. The main feature of the normal state is that $1/T_1T$ decreases monotonically with increasing temperature, as shown by the dashed line, which is a guide to the eye. In the superconducting state, a drop in $1/T_1T$ is observed. The solid line is a phenomenological fit to the formula

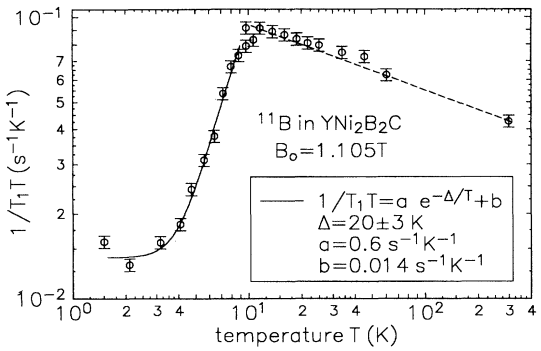

FIG. 3. ^{11}B spin-lattice relaxation as a function of T. The rise in $1/T_1T$ with decreasing T (the corresponding dashed line is a guide to the eye) in the normal state is anomalous.

$1/T_1T=a\ \exp\{-\Delta/T\}+b$, with $\Delta=20$ K, $a=0.6$ $(\mathrm{sK})^{-1}$, and $b=0.014$ $(\mathrm{sK})^{-1}$.

IV. DISCUSSION

Our measurements of the ^{11}B spectra indicate that there is an axially symmetric electric field gradient at the B site in YNi_2B_2C with $\omega_Q/2\pi=(355\pm10)$ kHz and that the main contribution to the Knight shift is isotropic, with a normal-state value $K_i=+(5.7\pm0.7)\times10^{-4}$ at 300 K that decreases linearly $(15\pm15)\%$ as T is lowered to 11 K. Although this value for K is typical for B in intermetallic compounds,[7,11] the dominance of the isotropic part of the Knight shift is unusual, because the main contribution to boron hyperfine interaction is usually from p-electron states that contribute only to the anisotropic part of the hyperfine interaction. This result could signify that there is an important transferred hyperfine interaction (isotropic) or an unusually large boron s-electron character to the states at the Fermi energy.

When it is considered along with the weak decrease with temperature of K_i, the behavior of $1/T_1T$ in the normal state (Fig. 3) is anomalous for a metal in which the nuclei are relaxed by hyperfine fluctuations of the contact hyperfine interaction with electrons in a wide band (Korringa relaxation). For this circumstance, T_1TK^2 is a constant whose value is $(\hbar\gamma_e^2)/(4\pi k\gamma_n^2)=2.51\times10^{-6}$ sK for ^{11}B and non-interacting electrons with $g=2$ (γ_e and γ_n are the electron and nuclear gyromagnetic ratios, $\hbar$ is Planck's constant, and k is Boltzmann's constant). Our experimental value at 300 K is 7.6×10^{-6} sK. The closeness of the two values indicates that the mechanism for $1/T_1$ is the hyperfine interaction with band electrons. Such deviations from the free electron value are usually attributed to electron interactions and a different g value for the conduction electrons. The observed increase of $1/T_1T$ and small decrease of K_i with decreasing T implies a modest slowing of the conduction electron spin dynamics at finite wave vector with little or no change in the uniform susceptibility of the band electrons, perhaps associated with the two-dimensional sheets of Ni ions in this material. Alternatively, it may be associated with sharp features in the density of states near the Fermi energy calculated for the nearly identical material $LuNi_2B_2C$.[6] (We do not consider quadrupolar relaxation by phonons[12] because the measured relaxation rate has a temperature dependence that is incompatible with it.)

The qualitative behavior of $1/T_1T$ in the superconducting state shows the drop usually associated with the reduced concentration of the thermally excited quasiparticles that relax the nuclear spins. It is, however, terminated at about $0.4T_c$ and no Hebel-Slichter peak is present. It is tempting to view the functional form of the solid line that fits the data as a total relaxation rate that is a sum of relaxation by quasiparticles with a uniform gap away from the vortex cores, Korringa relaxation in the cores, and rapid spin diffusion between spins inside and outside the vortex cores.[13] However, substantially more work is needed to establish whether this model truly applies to YNi_2B_2C, especially since the behavior in the normal state is anomalous. Also, this analysis does not take into account anisotropic properties of the material and is based upon measurements made with a powdered sample of randomly oriented particles.

The second moment formula of Pincus *et al.*[14] can be used with our measurement of ΔB to obtain the penetration depth (λ) of YNi_2B_2C:

$$\lambda=\sqrt{\Phi_0/22.3\Delta B}, \tag{1}$$

where Φ_0 is the flux quantum $(2.07\times10^{-7}\ \mathrm{G\,cm^2})$. Substitution of the measured value of ΔB obtained at 1.5 K gives $\lambda(0)=(108\pm5)$ nm. This value represents a powder average; it does not take into account possible anisotropic properties of the superconductor.

This measurement of λ, which is based upon the magnetic field distribution within the sample, is somewhat smaller than the value 150 nm deduced from thermodynamic measurements by Xu *et al.*[3] When combined with their value 10 nm for the coherence length, a Ginzburg-Landau parameter $\kappa=10$ is obtained; i.e., YNi_2B_2C is not a strongly type-II superconductor.

Finally, we point out that the reduction of the magnetic field in the sample by its magnetization at $T/T_c=0.3$ and our measuring field of 1.1 T can be estimated by using the linear approximation[15] for the magnetization ($\mathscr{M}$) of a type-II superconductor as a function of the applied magnetic field ($\mathscr{H}$) well above the lower critical field (SI units),

$$\mathscr{M}(\mathscr{H})=-\frac{1}{2\kappa^2}(H_{c2}-\mathscr{H}), \tag{2}$$

where H_{c2} is the upper critical field. The corresponding local field in a particle must be modified by the effective demagnetization factor N_{eff}, which accounts for the particle shape, the overall shape of the sample, and the filling factor of the powdered sample. We estimate that for our sample, $N_{\mathrm{eff}}\simeq0.5$. Substitution of the values $\kappa=10$, $H_{c2}=3.5T$,[4] and $B_0=1.1$ T gives a fractional change in field of -0.5%. The closeness of this estimate to our observed value -0.3% for this quantity is the justification of our earlier statement that nearly all of the shift of the centroid of the NMR line in the superconducting state is caused by the sample magnetization.

V. CONCLUSIONS

We have reported measurements of the ^{11}B NMR spectrum, Knight shift, and spin-lattice relaxation rate in the nor-

mal and superconducting states of the quaternary superconductor YNi_2B_2C [zero field $T_c=(15\pm0.5)$ K]. The boron site has an axially symmetric electric field gradient with a quadrupolar interaction parameter $\omega_Q/2\pi=(1/8\pi)e^2qQ = (355\pm10)$ kHz and an isotropic Knight shift that has a small, linear decrease from $(+5.7\pm0.7)\times10^{-4}$ at 300 K to $(+4.9\pm0.7)\times10^{-4}$ at 11 K. The anisotropic part of the Knight shift is much smaller than the isotropic part. An anomalous decrease of $1/T_1T$ in the normal state is seen that suggests a slowing of the correlation time that characterizes the electron-nuclear hyperfine interaction. An analysis of the increase in the NMR linewidth with decreasing temperature in terms of the field variation of the vortex structure yields $\lambda(0)=(108\pm5)$ nm for the low-temperature limit of the penetration depth. A sharp reduction in $1/T_1T$ occurs at the superconducting transition and no Hebel-Slichter peak is seen.

Recently, we became aware of similar measurements by Borsa *et al.*[16] There is substantial agreement between our results and theirs.

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