Electronic States of Boron in Superconducting MgB$_2$ Studied by $^{11}$B NMR

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NMR spectra and nuclear spin-lattice relaxation rate $T_1^{-1}$ of $^{11}$B have been measured in superconducting polycrystalline MgB$_2$ with $T_c^\text{ons}$ $\approx$ 39.5K. It is shown that $(T_c T_1^{-1})$ and the Knight shift $K_s$ are independent of temperature and nearly isotropic above $T_c$. Both of these quantities are decreased gradually in going to superconducting state. According NMR data the density of states (DOS) near the Fermi level is flat at the scale $\approx$ 500K. Some conclusions on the orbital content of the DOS at the Fermi level was done and compared with the results of the band structure calculations.

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Discovery of superconductivity in magnesium diboride MgB$_2$ showing remarkable high temperature of superconducting transition ($T_c$ $\approx$ 40K) stimulated intensive studies of the electron properties of this new medium. The group symmetry $D_{6h}$ is well known and relates to the hexagonal AlB$_2$-type. Boron forms a primitive honeycomb lattice and pronounced $B-B$ covalent bonding creates graphite-like sheets of boron separated by hexagonal layer of Mg. Calculations of electronic band structure show that the bands near the Fermi level are derived mainly from 2$p_{x,y}$ bonding orbitals of boron. As predicted the dispersion of these bands is extremely small near the $\Gamma$ point of the Brillouin zone. They form two small cylindrical Fermi surfaces around $\Gamma-A$ line. Due to their 2D character they contribute more than one third of the total DOS - $N(0)$$_{\text{Sr}}$=0.199 (eV at.B)$^{-1}$. Sizeable electron-phonon coupling is predicted for electrons in these 2$p_{x,y}$ bands and strong boron isotope effect reported in $^{11}$B is in favor that MgB$_2$ being phonon mediated superconductor. Electron-phonon coupling constant is proportional to DOS at the Fermi level and it is quite important to have experimental estimations of this quantity in MgB$_2$.

We have measured NMR line shift ($K$) and nuclear spin-lattice relaxation rate ($T_1^{-1}$) of $^{11}$B. For boron in metallic MgB$_2$ both these quantities contain the contributions determined by hyperfine coupling with conduction electrons of s and p bands. The hyperfine fields of s-electrons leads to isotropic contributions to the Knight shift ($K_s$) and ($T_1^{-1}$). While hyperfine coupling with conduction electrons of p bands leads to anisotropic contribution both to the NMR line shift ($K_{a\ell}$) and the nuclear spin-lattice relaxation rate of $^{11}$B. This anisotropic contribution to ($T_1^{-1}$) depends on the orbital content of $2p_i$ electrons, having near the Fermi energy appropriate DOS $N_i = f_i * N(E_F)$.

Polycrystalline MgB$_2$ was prepared using a mixture of magnesium chips and amorphous boron pressed into pellets and placed in a tantalum crucible. The pellets were subjected to a two step annealing in purified helium flow at temperatures $P_0$ $\approx$ 800C for 1 hour and resulting phase content was the following: MgB$_2$ (78.6%); Mg(16.6%); MgO (4.7%) BN (traces). After succeeding annealing at $T_{an}$=785C for 1 hour (evaporation of magnesium) the final phase content was obtained: MgB$_2$ (89.9%); MgO (5.2%); BN (1.7%). Quantitative phase analysis of the samples was carried out using X-ray powder diffraction data collected with a STADI-P diffractometer (STOE, Germany) and PDF2 data base (ICDD, USA). AC magnetization measurements show the SC transition with $T_c^\text{ons}$ = 39.5K and $\Delta T_c$ = 2.5K.

NMR measurements were carried out on a pulse spectrometer over the temperature range of 5-300K in magnetic fields $H_0$ = 2.1 and 9.1 T. The spectra were obtained by Fourier transformation of the second half of the spin-echo signal followed the $(\pi/2)_x - \tau_{del} - (\pi)_x$ pulse sequence. The broad spectra exceeding the frequency band excited by rf-pulse were measured by summation of an array of Fourier-signals of an echo accumulated at different equidistant operating frequencies. The components of magnetic shift tensor ($K_{iso}, K_{a\ell}$) for $^{11}$B ($I=3/2$) as well as the electric field gradient (EFG) parameters - quadrupole frequency $\nu_Q$ and asymmetry parameters $\eta$ - were determined by computer simulation of the measured NMR spectra. The powder pattern simulation program takes into account the quadrupole coupling corrections up to the second order of the perturbation theory. Positions of the features of both central line (transition $m = -1/2 \leftrightarrow +1/2$) and satellite lines (transitions $m = \pm 1/2 \leftrightarrow \pm 3/2$) were involved in consideration. The diamond form of BN was used as a reference.

The boron atoms in MgB$_2$ unit cell are located at the sites with the axial symmetry of the nearest environment. The $^{11}$B nucleus has a spin $I=3/2$ and electric quadrupole moment $Q$ = 0.04065 $\cdot$ $10^{-24}$ cm$^2$. Thus the resonance frequency of $^{11}$B NMR-probe is determined by both hyperfine magnetic interaction and the interaction of quadrupole moment with electric field gradient (EFG) $V_{zz}$, created at the nuclear site by the electronic and ionic environments.
The NMR spectrum of $^{11}$B including all transitions is shown in Fig. 1 for $T = 300$K. Simulation of the powder patterns NMR line shape allowed us to determine with a reasonable accuracy spherical components of the magnetic shift ($K_{iso}$, $K_{az}$) and the EFG ($\nu_Q, \eta$) tensors: $K_{iso}=175(15)$ ppm, $K_{az} < 30$ ppm; $\nu_Q = \frac{3Q}{2(2-I)}V_{zz} = 0.828(10)$ MHz; $\eta=0$. The measurements at different $T$ have demonstrated that magnetic shift and EFG parameters are independent of temperature in normal state down to $T_c(H)$ (see Fig. 2). Similar observation for magnetic shift of the $^{11}$B NMR central line was reported recently in Ref. [1].

Magnetic shift is decreased gradually in going to superconducting state and at $T = 20$K$\approx T_c/2$ its magnitude becomes close to zero. Unfortunately we can not evaluate precisely the magnitude of the Knight shift from the data obtained, since additional diamagnetic contribution due to supercurrents arisen around vortexes should be involved into consideration. At present time one may conclude that $K_s(20$K) is less than 100 ppm.

Nuclear spin-lattice relaxation rate of $^{11}$B was measured using the inversion-recovery technique and working at the frequency domain. Amplitude of rf magnetic field in the pulse exceeded 100 Oe. The measurements were performed at different point of spectrum to study anisotropy of $T_1(\theta)$. Here $\theta$ is the angle between c-axis and $\mathbf{H_0}$. The measurements at the peak of central line give the angle-averaged magnitude of $T_1$. In this case $T_1$ was determined by fitting $m(t)$ data to the following expression [10]:

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

In measurements at a peak $(c \perp \mathbf{H_0})$ and a step $(c \parallel \mathbf{H_0})$ of the high-frequency satellite powder pattern (see inset in Fig. 3) the magnitude of $T_1$ was determined by fitting $M(t)$ data to the another expression [11]:

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

The temperature dependence of the product $(T_1T)^{-1}$ measured at the central line is shown in Fig. 4. In the normal state the magnitude of $(T_1T)=155(5)$sK is found as independent of temperature. A slightly larger value of $(T_1T)$ was reported in Ref. [11] for bulk sample of MgB$_2$. Independent of temperature product $(T_1T)^{-1}$ may be considered as an evidence for a flatness of the $N(E)$ curve near the Fermi energy at the scale of ~500K.

A rather unexpected result is obtained in measurements of $T_1$ at the crystallites which c-axis is differently oriented with respect $\mathbf{H_0}$. As seen at Fig. 3 the $M(t)$ data being measured at differently oriented crystallites are fitted well to the expression (2) with the very same adjustable parameter $T_1$. Corresponding magnitude of the product $(T_1T)=155(5)$sK as was obtained for central line. Using the results of band calculations we expect to find the ratio $T_1(c \perp \mathbf{H_0})/T_1(c \parallel \mathbf{H_0}) \approx 1.2$, if to assume that nuclear spin lattice relaxation rate is monitored exclusively by hyperfine dipolar and orbital interaction between nuclear magnetic moment and p-electrons of the partly filled $p_{x,y}$ bands. The results obtained means that $T_1^{-1}$ is determined by the Fermi contact interaction with conducting electrons of s-band or both of three partial $p_i$ DOS are equal ($f_x=f_y=f_z$).

At temperature below $T_c$ nuclear spin-lattice relaxation rate deviates of the Korringa behavior. No evidences for the Hebel – Slichter [11] coherence peak was seen in measurements near $T_c$ at external field of 2.1T. At temperature below 20K we approximated $T_1$ data by expression in the thermally-activation exponential form and found the ratio $2\Delta/k_BT_c > 2.5$ assuming isotropic magnitude of the superconducting energy gap in MgB$_2$.

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FIG. 2: The temperature dependence of $^{11}K_{iso}$ measured at the external fields of 9.123T (○) and 2.113T (●). The value of $T_c$ in the field is pointed out by an arrow.

FIG. 3: Recovery of $^{11}$B nuclear magnetization in measurements of $T_1$ using the inversion-recovery pulse sequence. Irradiated regions of the $^{11}$B spectrum related to the crystallites which c-axis is differently oriented with respect to $H_0$ are shown in inset.

FIG. 4: The temperature dependence of $(^{11}T_1T)^{-1}$ product vs $T$ in MgB$_2$ measured at the external magnetic fields of 9.123T (○) and 2.113T (●). The dotted straight line is a guide for the eyes to show that the product $T_1T$ is independent of $T$. 
T=300K
$T_C$ in 2.113 Tl

$T_C$ in 2.113 Tl

$T_C$ in 2.113 Tl

$T_C$ in 2.113 Tl

$T_C$ in 2.113 Tl

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