Reduction in the electron density-of-states in superconducting MgB$_2$ disordered by $n^1$-irradiation: the $^{11}$B and $^{25}$Mg NMR estimates

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NMR line shift and nuclear spin-lattice relaxation rate $T_1^{-1}$ of $^{11}$B and $^{25}$Mg were measured in superconducting MgB$_2$ ($T_{c}^0=38K$) structurally disordered by nuclear reactor neutrons up to the fluence of thermal neutrons $\Phi = 1 \cdot 10^{19}$ cm$^{-2}$. The temperature of superconducting transition was shifted down to $T_{c}^{\text{irrad}}=7K$ under irradiation. The change due irradiation in the partial electron density of states (DOS) at the Fermi energy of boron and magnesium were traced by taking into account that $T_{c}^{-1}$ of $^{11}$B and $^{25}$Mg are determined by hyperfine magnetic interactions with carriers. It was revealed that electronic states near $E_F$ of Mg are influenced negligibly by irradiation whereas partial DOS of the 2$p_{x,y}$ states reduces greatly in irradiated MgB$_2$. According to the Mc Millan formula, NMR data show that critical temperature decreases in irradiated MgB$_2$ mainly due to reduction in the partial DOS of p states of boron.

PACS numbers: 74.25.-q, 74.72.-b, 74.60.-k, 74.60.Es

I. INTRODUCTION

Discovery of superconductivity in magnesium diboride MgB$_2$ showing high temperature of superconducting transition ($T_c \sim 40K$) [1] stimulated extensive studies of its electron properties. Layered crystal structure of MgB$_2$ (space group symmetry $D_{6h}$) is well known and relates to the hexagonal AlB$_2$-type [2]. Boron forms a primitive honeycomb lattice and pronounced B-B covalent bonding creates graphite-like sheets of boron separated by hexagonal layer of Mg and interatomic bonding is much more metallic in origin. Recent first principles calculations of electronic band structure show that the bands near the Fermi energy are formed mainly from 2$p_{x,y}$ bonding orbitals of boron [14, 15, 16]. As predicted the dispersion of these bands is extremely small near the $\Gamma$ point of the Brillouin zone. These bands form two small cylindrical Fermi surfaces around $\Gamma$-A line. Due to their 2D character they contribute near the Fermi energy more than one third of the total DOS $N(2p_{x,y})=0.072(eV\text{-spin-of B})^{-1}$ [3]. Sizeable electron-phonon coupling $\lambda \sim 0.75 - 0.87$ is predicted for electrons in these 2$p_{x,y}$ bands and strong boron isotope effect reported in [3] is in favor that MgB$_2$ being phonon mediated superconductor. The parallels regarding to band structure of MgB$_2$ and intercalated graphite were enlightened in [3, 4, 14]. An interplay between 2D covalent in-plane ($\sigma$) and 3D metallic-type ($\pi$) conducting bands accompanied by corresponding ($\sigma \leftrightarrow \pi$) charge transfer was considered as important factor determining electronic properties and superconductivity in MgB$_2$.

The influence of structural disorder on the electron states in conduction band of MgB$_2$ is question of great interest both in physics and technology. As known high-pressure technology in sintering of the compacted MgB$_2$-materials results in stressed crystal structure accompanied by decrease of $T_c$ and broad superconducting transition in comparison with as grown at ambient pressure crystals. Radiation disordering by neutrons is probably the purest method to study the influence of the induced structural disorder on the physical properties regarding to the motion of carriers in conduction band. As shown in [15] superconducting temperature $T_c$ drops below 10K whereas the initial crystal structure is preserved under $n^1$-irradiation up to the fluence of thermal neutrons $\Phi = 1 \cdot 10^{19}$ cm$^{-2}$. The moderate irradiation leads to anisotropic expansion of the crystal lattice with increase of the $c/a$ ratio resulting in increase of the interlayer distance. The Rietveld analysis refinement of X-ray diffraction patterns yields some decrease in the occupation number at Mg-sites.

NMR line shift and nuclear spin-lattice relaxation rate (NSLRR) $T_1^{-1}$ studies give an unique opportunity to probe electronic states near $E_F$ through static and fluctuating parts of hyperfine magnetic fields created by carriers at the nuclei. Near a given NMR probe the wave function of carriers might be considered as the atomic-like. This permit to analyze the orbital content of the carrier states and to estimate contributions of different atoms to the total DOS near $E_F$. Similar detailed consideration of the experimental data regarding $T_1^{-1}$ of $^{11}$B in structurally ordered MgB$_2$ [3, 12, 13] was presented in [3, 12] on the basis of band calculations and it was concluded that the orbital hyperfine interaction of 2$p$-holes with nuclear magnetic moments should dominate in NSLRR of $^{11}$B. This contribution to $^{11}$B$T_1^{-1}$ is proportional to $N(2p_{x,y})^2$ and depends on the orbital content of 2$p$ electrons, having appropriate DOS $N_i = f_i \ast N(E_F)$ near the Fermi energy [3, 12]. As shown in [2] the Fermi-contact interaction should be responsible for the Knight shift and NSLRR of $^{25}$Mg in MgB$_2$.

We have measured the NMR line shift and nuclear spin-lattice relaxation rate of $^{11}$B and $^{25}$Mg in the ordered unirradiated ($T_{c}^{\text{unset}}=38K$) and disordered by $n^1$-irradiation ($T_{c}^{\text{irrad}}=7K$) MgB$_2$ to study the change in DOS of the conduction bands.
II. EXPERIMENTAL RESULTS AND DISCUSSION

Irradiation of polycrystalline sample was performed in nuclear reactor IVV-2M at $T \sim 350$ K up to the fluence of thermal neutrons $\Phi = 1 \times 10^{18}$ cm$^{-2}$, and of fast neutrons, to $5 \times 10^{18}$ cm$^{-2}$ (total dose - of more than 10 dpa). Superconducting transitions measured by AC susceptibility for ordered and irradiated samples of MgB$_2$ are shown in Fig.1.

NMR measurements were carried out on a pulse spectrometer over the temperature range of 20-300K in magnetic field 9.1T. The spectra of $^{11}$B and $^{25}$Mg 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 $\delta \nu$ was taken about the total width of the NMR spectrum including all of transitions for powder sample ($^{25}\delta \nu \sim$ 1MHz, $^{25}\delta \nu \sim$ 2MHz). Being applied during an interval $t << T_1$ this broad-band saturating sequence of rf pulses equalizes nicely populations of magnetic levels in the spin systems of $^{11}$B($^{11}$I=3/2) and $^{25}$Mg($^{25}$I=5/2) showing the nonequidistant energy splitting in magnetic field.

As a result we obtained that in ordered sample of MgB$_2$ (see Fig.2) the recovery of nuclear magnetization $M_Z(t)$ follows to the single-exponential law: $M_Z(t) \sim (1 - \exp(-t/T_1))$. Using this experimental procedure for $T_1$-measurements in irradiated sample we have an opportunity to analyze the distribution in NSLLR arisen due structural disorder. Indeed in irradiated MgB$_2$ (see Fig.2) a part of the $^{11}$B nucleus ($\sim (0.07 - 0.08)$ of total amount) shows the rate of spin-lattice relaxation reduced in a factor of 10 as compared with the ordered sample. It is believed that these slow-relaxing nuclei might belong to boron sited in neighborhood of the $n^1$-tracks where the short-range atomic order is much more influenced in comparison with atoms of B sited in the base volume fraction of the irradiated MgB$_2$.

A. $^{25}$Mg NMR

Magnetic shift of $^{25}$Mg NMR line is found as positive isotropic quantity in normal state of the ordered MgB$_2$. Its value $^{25}K_{iso} = 280(30)$ ppm does not change with temperature in the range 20-300K ($T_c(9T) < 15$K [1]). In NSLLRR measurements of $^{25}$Mg it was found that product $^{25}(T_1 T)$ is also independent of temperature above $T_c$ and equals $^{25}(T_1 T) = 350(30)$ sec-K. Magnetic shift of $^{25}$Mg in MgB$_2$ consists of two base parts, the chemical shift $^{25}\delta$ and the Knight shift $^{25}K_{sp}$. As shown in [12] the Fermi-contact interaction of $^{25}$Mg with carriers of conduction

![FIG. 1: AC-susceptibility superconducting transition curves for ordered (1) and $n^1$-irradiated (2) samples of MgB$_2$.](image1)

![FIG. 2: Recovery of $^{11}$B nuclear magnetization $^{11}M_Z(t)$ shown in semi-log scale of the quantity $^{11}m(t) = (M_Z(\infty) - M_Z(t))/M_Z(\infty)$ versus time interval $t$ after applying broad-band saturating comb of rf pulses to the ordered (open circles) and irradiated (closed circles) samples of MgB$_2$($T = 100$K).](image2)
band should dominate both in $^{25}K_{sp}$ and $^{25}T_1^{-1}$. The independent of temperature behavior of $^{25}K_{sp}$ and $^{25}T_1^{-1}$ is in favor of this prediction and demonstrate that DOS near $E_F$ is flat at the energy scale exceeding 0.1eV. Applying for s-states of Mg an approximation of the free electron gas we estimated $^{25}K_{sp} = 470$ ppm using appropriate form of the Korringa relation $^{[13]}
abla$

$$25(T_1TK_{sp})/S = 2\mu_B^2/25\gamma^2\hbar k_B; S = 1$$ (1)

Correspondingly the chemical shift of $^{25}$Mg in ordered MgB$_2$ might be estimated as $^{25}\delta = -190$ ppm.

In irradiated sample total NMR shift decreases slightly towards $^{25}K_{iso,irrad} = 240(30)$ ppm and within accuracy of $^{25}T_1$-measurements the product $^{25}(T_1T) = 360(80)$ sec-K is nearly the same as before irradiation. This means that for the base part of the sample the contribution of Mg(s) states to the total DOS is influenced negligibly by structural disorder induced during $n^1$-irradiation.

**B. $^{11}$B NMR**

The NMR spectra of $^{11}$B including all transitions are shown in Fig. 3 for $T = 100$K both for ordered ($\Phi = 0$) and irradiated ($\Phi = 1 \cdot 10^{19}$cm$^{-2}$) samples of MgB$_2$. The spectrum is additionally broadened under irradiation due to the distribution of magnetic shift ($\Delta K \approx 40$ ppm for central line) and quadrupole frequency ($\Delta\nu_Q \approx 100$ KHz for satellite lines). Spherical components of the magnetic shift ($^{11}K_{iso}$, $^{11}K_{ax}$) and the EFG ($^{11}\eta,^{11}\eta$) tensors were determined by simulating the powder patterns NMR line shape and data obtained are listed in Table 1. 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) for both structural states of MgB$_2$. Substantial decrease of $^{11}K_{iso}$ occurs in irradiated sample, $^{11}K(\Phi = 0) - ^{11}K(\Phi = 1 \cdot 10^{19}$ cm$^{-2}$) =70 ppm.

The total NMR line shift of $^{11}$B might be separated in two parts.

$$^{11}K = ^{11}\delta + ^{11}K_{sp}$$ (2)

The chemical shift $^{11}\delta$ is due to hyperfine magnetic fields originating from the orbital motion of electrical charges in applied external magnetic field. The Knight shift $^{11}K_{sp}$ is determined by hyperfine interactions of nuclei with magnetic moments associated with the electron spin of carriers in the conduction band $^{[16]}$. Here we consider only an isotropic part $^{11}K_{sp,iso}$ of the Knight shift, which is contributed by the Fermi-contact interaction with conducting s-electrons ($^{11}K_s$) and the hyperfine core polarization effects ($^{11}K_{cp}$) of B(2p)-electrons occupying states near $E_F$.

$$^{11}K_{sp,iso} = ^{11}K_s + ^{11}K_{cp}$$ (3)

Either of these contributions is proportional to the density of states in corresponding bands.

According the $^{25}$Mg NMR data the partial DOS of the Mg(s)-states is roughly unchanged by induced disorder. It is reasonable to assume that the Fermi-contact term $^{11}K_s$ is also insensitive to to the gain of structural disorder considered in this work

An estimate of the core-polarization Knight shift was performed in $^{[12]}$ as a result of $ab$ initio calculations and it was shown that $^{11}K_{cp,calc} = -7$ ppm is negative and $^{11}K_{cp} < ^{11}K_s \approx 30$ ppm for boron in MgB$_2$. We are far from the opinion that real magnitude of $^{11}K_{cp}$ should deviate strongly from the calculated in $^{[12]}$.

Induced disorder might influence paramagnetic contribution $^{11}\delta_{orb}$ to the total chemical shift of $^{11}$B. The term $^{11}\delta_{orb}$ arises as the second-order perturbation effect of magnetic field on the orbital motion of electrons in partially filled $2p_{x,y}$ bands. Crude estimate of this term $^{11}\delta_{orb} \approx 2\mu_B < r^{-3} >_{2p} / W \sim 200$ppm might be obtained using $< a_0 / r^3 >_{2p} = 1.1$ $^{[12]}$ and $W \sim 2$eV (a$_0$ is the Bohr radius and $W$- the width of $2p_{x,y}$ conducting band near $\Gamma$-A line $^{[3] - [5]}$). An increase of $W$ due the induced disorder might result in decrease of $^{11}\delta_{orb}$ which,

![FIG. 3: $^{11}$B NMR spectra of ordered (Φ = 0) an n$^1$-irradiated (Φ = 1$\cdot 10^{19}$cm$^{-2}$) MgB$_2$ measured in the magnetic field of 9.123T at T=100K.](image-url)
as believed, determines in main the variation of $^{11}$K under irradiation. Of course in support of this assumption it will be desirable to have the much more precise estimates for $^{11}$\delta_{orb} obtained as a result of the band calculations.

It is more reliably to trace the reduction in partial DOS of 2p-states in irradiated MgB$_2$ considering the ($^{11}$T$_1$T)$^{-1}$ data (see Fig.4). In the normal state the product ($^{11}$T$_1$T) is found as independent of temperature both in the ordered ($^{11}$T$_1$T)= 155(5) sec-K and irradiated ($^{11}$T$_1$T) =250(20) sec-K samples. As for $^{25}$Mg an independent of temperature product ($^{11}$T$_1$T)$^{-1}$ may be considered as an evidence for a flatness of the $N(E)$ curve near the Fermi energy at the scale of $\sim$1000K.

As shown in [10, 11] the orbital relaxation mechanism dominates in spin-lattice relaxation rate of $^{11}$B in MgB$_2$. According to [12, 13] we have the following expression for isotropic part of ($^{11}$T$_1$T)$_{orb}$:

$$
(11T1T)_{orb}^{-1} = \frac{16}{3}m_B^2(11\gamma)^2\hbar k_B <r^{-3}>_{2p}N_{2p}(E_F)^2[f_x(f_x+2f_z)]
$$

The orbital NSLRR is proportional to $N_{2p}(E_F)^2$ and depends on the orbital content of 2p electrons, having near the Fermi energy appropriate DOS $N_i = f_i*N(E_F)$.

Using expression (4) and the ($^{11}$T$_1$T)-data listed in Table 1 we find that the partial 2p DOS near $E_F$ in irradiated MgB$_2$ is decreased by a factor 0.75 in comparison with its magnitude in the ordered unirradiated sample. According the Mc Millan formula the effect of reduced $N_{2p}(E_F)$ results in suppression of the superconducting transition temperature down to $T_c = 10$K. A little bit less temperature of superconducting transition $T_{c\text{\scriptsize \textit{onset}}} = 7$K was revealed in AC susceptibility measurements.

At lasts an average magnitude of the quadrupole frequency $^{11}\nu_Q = e^{11}QV_{zz}/2h$ is found to decrease slightly under disorder. The boron electric field gradient $V_{zz}$ is defined by anisotropy in the electron occupancies $p_i$ of B 2p bands in the following manner [18]

$$
V_{zz} \approx p_z - (p_x + p_y)/2
$$

The reduced value of $^{11}\nu_Q$ in irradiated sample might be considered in favor of the redistribution in occupancies of B 2p bands resulting in the more filled $2p_{x,y}$ bands of MgB$_2$ disordered by neutron irradiation.

**III. CONCLUSION**

An influence of structural disorder induced by n$^1$-irradiation up to thefluence of thermal neutrons (Φ = 1 · 10$^{19}$cm$^{-2}$) on the density of the electron states (DOS) near the Fermi energy was studied in MgB$_2$ by measuring NMR line shift and nuclear spin-lattice relaxation of $^{11}$B and $^{25}$Mg. According the NMR data obtained

- the partial DOS of s-states is not influenced by disorder;
- substantial decrease in DOS of 2p-states occurs under irradiation;
- an effect of the reduced 2p-DOS dominates in suppression of the superconductivity in MgB$_2$ structurally disordered by neutron irradiation.

**Acknowledgments**

The authors are grateful to Dr.V.G.Zubkov, Dr.T.V.D’yachkova and Dr.A.P.Tyutyunnik for providing sample of MgB$_2$. Work is supported by the Russian State contract No107-1(00)-P/order No22/ and Russian State Program of Support of Leading Scientific Schools ( project No 00-15-96581).

**Table I:** The unit cell parameters, the $^{11}$B NMR shift and the quadrupole coupling parameters of boron and $T_c$ in the ordered and $n^1$-irradiated MgB$_2$

| MgB$_2$ | Φ = 0 | Φ = 1 · 10$^{19}$cm$^{-2}$ |
|---------|--------|--------------------------|
| a, nm   | 0.30878| 0.30953 |
| c, nm   | 0.35216| 0.35533 |
| a/c     | 1.140  | 1.148  |
| $T_{c\text{\scriptsize \textit{onset}}}$, K | 38     | 7      |
| $^{11}$K$_{1\text{\scriptsize \textit{iso}}}$, ppm | 100(10) | 30(15) |
| $^{11}$K$_{1\text{\scriptsize \textit{iso}}}$, ppm | 30(5)  | 0-20   |
| $^{11}$ν$_Q$, KHz | 828(10) | 790(20) |
| $^{11}$η | 0.0    | 0.0-0.1 |
| $^{11}$T$_1$T, sec-K | 155(5) | 250(20) |
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