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Influence of Rb, Cs and Ba on superconductivity of magnesium diboride

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Magnesium diboride has been thermally treated in the presence of Rb, Cs, and Ba. Magnetic susceptibility shows possible onsets of superconductivity in the resulting samples at 52 K (Rb), 58 K (Cs) and 45 K (Ba). Room-temperature ^{11}B NMR indicates to cubic symmetry of the electric field gradient at boron site for the samples reacted with Rb and Cs, in contrast to the axial symmetry in the initial MgB_2 and in the sample treated with Ba.

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Recent discovery of superconductivity in magnesium diboride, MgB_2, with $T_c \simeq 39$ K [1] has stimulated intensive study of this material. Its simple chemical composition, high symmetry of crystal lattice ($P6/mmm$) and hence high symmetric electronic structure [2] have enabled fine calculations to clarify the mechanism of high temperature superconductivity in MgB_2 [3].

It has been reported previously that doping MgB_2 with carbon [4], Li [5, 6], Be [7], Zn [8], Al [6, 9], Ti [10], Ni, Fe, Co [11], Mn [12], and Si [6] only reduces the superconducting transition temperature. No information has been reported so far about doping of MgB_2 with heavier alkali and alkali-earth metals. These elements are capable of strong carrier donation to the electron system and may therefore essentially enhance superconducting properties of the host material. In this paper we report on the influence of Rb, Cs and Ba on superconductivity of MgB_2.

MgB_2 was thermally treated with Rb, Cs and Ba through liquid-phase reaction. The reacted samples are hereafter nicknamed as &Rb, &Cs, and &Ba samples. Two types of initial material were used: One contained 0.2–1 mm size granules of sintered in 1:1 molar ratio mixture of MgB_2 and Mg (MgB_2/Mg). The other one was fine powder of pure MgB_2. The initial material was vacuum sealed with the abundance of the metal (Rb, Cs or Ba) in quartz ampules preliminarily evacuated down to 10^{-3} Torr. The reactions were held with Rb and Cs for 10–100 hours at 160–300 °C, and with Ba for 5 minutes at 700 °C.

Superconductivity of the samples was studied by measuring the magnetic susceptibility, χ, in temperature interval 4.2–300 K. The low-frequency ac susceptibility was measured using a home-made set-up by means of a mutual inductance technique at frequency 623 Hz in a driving field ~ 0.1 Oe. The signal corresponding to the real part of χ was detected using a lock-in amplifier. Superconducting transitions of led, niobium, and BiSCO:2212 ($T_c = 90$ K) were used to insure fidelity of the temperature scale of the measurements, as well as for calibration of the diamagnetic response. In the case of Rb the measurements were made without unsealing the ampules to avoid sample oxidation. It also enabled to consecutively alter heat treatment and measurement on the same batch. The unreacted excess of the metal heat-linked the particles of the sample and the walls of the vacuumized ampule to provide correct measurement of the sample temperature.

To track the changes in the superconducting properties during the treatment of MgB_2 with an alkali metal, the reaction with Rb was performed through portions of heat treatment alternated by susceptibility measurements. Each time two samples were simultaneously exposed to the heat treatment, one containing MgB_2/Mg and the other one with pure MgB_2. Temperature dependencies of magnetic susceptibility, $\chi(T)$, measured between consecutive portions of heat treatment on MgB_2/Mg with Rb, are shown in Fig.1a. $\chi(T)$ of the host MgB_2/Mg sample before the heat treatment, depicted in curve *1*, has a sharp drop at 39 K denoting the superconducting transition at this temperature. Both the onset temperature and the width of the transition coincide with those of pure MgB_2[1]. Subsequent heat treatments with Rb lead to first increase of the transition onset temperature up to 52 K (curves *2* through *4*), and then rollback to 44 K (curves *5* through *7*)[13]. The sample that initially contained pure MgB_2 powder has retained the superconducting transition at $\simeq 39$ K during the whole sequence of heat treatment. Hence under the applied conditions of thermal treatment, ad-

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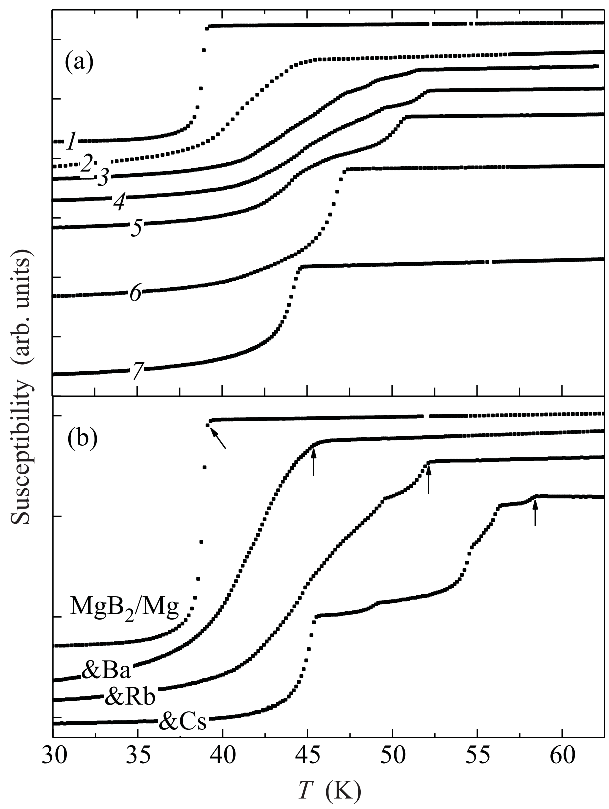

Fig.1. Temperature dependencies of magnetic susceptibility: (a) measured between consecutive heat treatments of MgB_2/Mg with Rb, *1* – initial sample, *2* – 10 hours at 180 °C, *3* – 13 hours at 190 °C, *4* – 15.5 hours at 200 °C, *5* – 36 hours at 200 °C, *6* – 56 hours at 200 °C, *7* – 18 hours at 300 °C; (b) the initial MgB_2/Mg, the one reacted with Ba (5 min. at 700 °C), with Rb (17 hours at 200 °C), and with Cs (20 hours at 160 °C followed by 100 hours annealing at 100 °C). Arrows indicate onsets of superconducting transitions

mixture of Mg to MgB_2 plays the key role in formation of the superconducting phase with T_c higher than in the host MgB_2.

Relying on the above results, the heat treatment regimes were adjusted for the reactions of MgB_2/Mg with Cs and Ba. Fig.1b shows $\chi(T)$ plots for &Cs and &Ba samples, as well as $\chi(T)$ for the initial MgB_2/Mg and for the &Rb sample. The $\chi(T)$ curves for &Cs and &Ba samples in Fig.1b deviate towards the diamagnetic state below 58 K and 45 K, respectively, indicating possible onsets of superconductivity. Therefore these results rise a question whether the superconducting transition temperature of the host MgB_2/Mg can be essentially enhanced through the reaction with Rb, Cs, or Ba.

The samples characterized in Fig.1b were subjected to ^{11}B NMR. The spectra were taken at room temperature in 7 T field using a Bruker MSL-300 spectrometer by means of the standard spin-echo technique with π pulse of $\simeq 4$ μs. Since ^{11}B NMR spectrum is known to be $\sim$ 800 kHz wide [14, 15] and the experiment bandwidth limited by the π-pulse length is $\sim$ 100 kHz, for each sample several spectra between 95 and 96.2 MHz at frequencies spaced by 100 kHz have been collected and added up. The resulting spectra are shown in Fig.2.

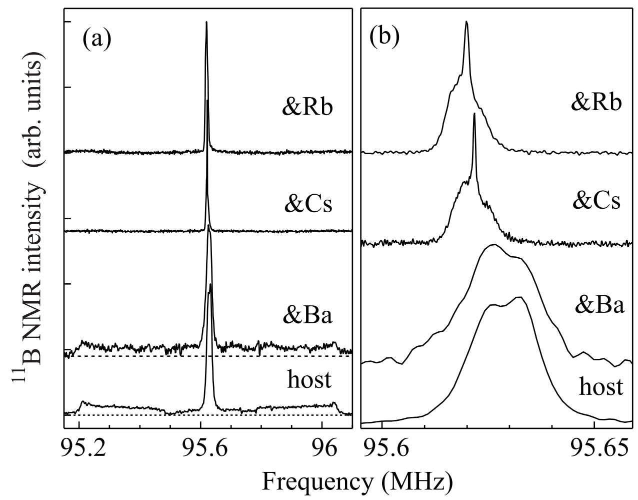

Fig.2. Room-temperature ^{11}B NMR spectra at 7 T in the host MgB_2/Mg and in MgB_2/Mg reacted with Ba, Cs, and Rb: The spectra in whole (a) and details of the central peaks (b)

It is known from previous studies [14, 15] that ^{11}B NMR spectrum in pure MgB_2 includes a sharp central peak and two broader satellite peaks separated by $\simeq$ 830 kHz. This kind of NMR spectrum originates from the spin 3/2 of ^{11}B and the axial symmetry of the charge environment of boron in MgB_2. The central peak corresponding to $(-1/2 \leftrightarrow 1/2)$ transition is close to the boron Larmour frequency, $^{11}\nu_L{=}^{11}\gamma H_0$, where $^{11}\gamma$ is ^{11}B gyromagnetic ratio and H_0 the external magnetic field. The satellites peaks $(\pm 3/2 \leftrightarrow \pm 1/2$ transitions) result from the quadrupole interaction of the nucleus with the charge environment in the crystal. At high (compared to quadrupole interaction) fields the distance between the satellites equals to the quadrupole frequency, ν_Q, proportional to the principal value of the electric field gradient (EFG) at the nucleus site, V_{zz} .

^{11}B NMR spectra in MgB_2/Mg and in MgB_2/Mg reacted with Ba (Fig.2a) agree with the results reported previously for pure MgB_2 [14, 15] including the same $\nu_Q \simeq 830$ kHz separating the satellites and the Pake doublet-topped central peak, Fig.2b, with $\simeq 17$ kHz full width at half maximum, FWHM. This infers that Ba essentially changes neither the axial symmetry nor the value of EFG at boron site. On the contrary, the spectra in the &Rb and &Cs samples differ strongly from that of the host MgB_2/Mg. First, the satellite intensities are much weaker and practically invisible in Fig.2a implying the presence of a phase with cubic symmetry of EFG at boron site with $V_{zz}=0$, besides the native axially symmetric phase. Comparison of the satellites and the central peak areas in MgB_2/Mg and in the &Rb and &Cs samples yields about 30% of the axially symmetric phase in the samples with alkali metals. Secondly, the central peaks in the &Rb and &Cs samples (Fig.2b) consist of an extremely narrow (FWHM$\simeq$ 1 kHz) feature on top of a wider (FWHM$\simeq$ 7 kHz) pedestal and are lower in frequency by $\simeq$8 kHz=84 ppm. Since the cental ^{11}B NMR peak in MgB_2 is broadened by the second-order quadrupole interaction [15], the smaller linewidth of the central peaks in the samples with alkali metals may also indicate to cubic symmetry of the EFG at boron site. More detailed analysis of the NMR data will be reported in a separate publication.

In the summary, the superconducting properties of MgB_2 reacted with Rb and Cs at 160–300°C, and with Ba at 700 °C have been studied. The compounds with apparent onset of superconducting transitions higher than in MgB_2 have been found for the samples that initially contained 1:1 mixture of MgB_2 and Mg. Room-temperature ^{11}B NMR has indicated to the presence of a phase with cubic symmetry of charge environment at boron site in the samples reacted with Rb and Cs, in contrast to the axially symmetric cases for the host MgB_2 and for the sample reacted with Ba.

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13. The curves shown in Fig.1 are reproducible and retain their shapes after a tenfold increase of the modulation frequency. Therefore the anomalies on the curves are not experimental artefacts but are related to the *ac* magnetic response of the samples. The response is diamagnetic upon cooling and its size is comparable with that of the reference sample (curve *1* in Fig.1). Since no other transitions, besides the superconducting one, are known to give diamagnetic response of this size, the observed anomalies have to be attributed to superconductivity.
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