Electron Transport in Diborides: Observation of Superconductivity in ZrB$_2$

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We report on syntheses and electron transport properties of polycrystalline samples of diborides (AB$_2$) with different transition metals atoms (A=Zr,Nb,Ta). The temperature dependence of resistivity, $\rho(T)$, and ac susceptibility of these samples reveal superconducting transition of ZrB$_2$ with $T_c = 5.5$ K, while NbB$_2$ and TaB$_2$ have been observed nonsuperconducting up to 0.37 K. $H_{c2}(T)$ is linear in temperature below T_c, leading to a rather low $H_{c2}(0) = 0.1$ T. At T close to T_c H_{c2} (T) demonstrates a downward curvature. We conclude that these diborides as well as MgB$_2$ samples behaves like a simple metals in the normal state with usual Bloch-Grüneisen temperature dependence of resistivity and with Debye temperatures: 280, 460 and 440 K, for ZrB$_2$, NbB$_2$ and MgB$_2$, respectively, rather than T^2 and T^3 as previously reported for MgB$_2$.

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The recent discovery of Akimitsu [1] of superconductivity in MgB$_2$ at 39 K has lead to a booming activity in physics community. It was reported that measurements of the upper critical field, $H_{c2}(T)$, and the thermodynamic critical field, $H_c(T)$, as well as the specific heat are all consistent with MgB$_2$ being a fairly typical intermetallic electron phonon mediated BCS superconductor with a superconducting transition temperature approximately twice that of a typical "metallic" superconductor. At the same time an unexpected T^2- and even T^3-normal state temperature dependence of the resistance has been reported [2, 3]. These results have initiated considerable interest to electron transport measurements and to a search for superconductivity in other diborides. Natural candidates for this search are AB$_2$-type light metals diborides (A = Li,Be,Al). However, up to now superconductivity has not been reported in the majority of these compounds [4–6]. Only very recently has superconductivity below 1 K ($T_c = 0.72$ K) been reported in BeB$_{2.75}$ [7]. According to Ref. [8], no superconducting transition down to 0.42 K has been observed in powders of diborides of transition metals (A = Ti, Zr, Hf, V, Ta, Cr, Mo, U). Only NbB$_2$ was found to be superconducting with very low $T_c = 0.62$ K. Since completing this work we have become aware of a recent paper [9] in which superconductivity was observed in TaB$_2$ at $T_c = 9.5$ K. This result contradict the data reported in this letter.

The crystal structure of diborides (ω phase [10]) can be viewed as a set of two-dimensional graphite-like monolayers of Boron atoms with honeycomb lattice, intercalated with A atoms monolayers forming ABAB heterostructure. It was proposed that superconductivity in

series of diborides of light metals (A=Be,Mg,Ca,Al) and a series transition metals (A=Ti,Zr,Hf,V,Nb,Ta) appear near a critical point in a strain and charge density phase diagram. An increase of the B-B distance larger than a critical value driven by A atom radii results in collapse of ideal ω phase into the trigonal rumpled ω phase. Lattice instability driven by both atom radii and charge densities may be a key reason why superconductivity appear in MgB$_2$ rather than in other diborides. This phase diagram suggests that ZrB$_2$ is a good candidate for superconductivity having strain close to the critical value (see [10]). In order to clarify whether this assumption is correct we studied the electron transport properties of ZrB$_2$, NbB$_2$, TaB$_2$ and MgB$_2$.

Polycrystalline samples of ZrB$_2$ and NbB$_2$ were obtained by conventional solid state reaction. Starting materials were Zr and Nb metal powders (99.99% purity) and sub-micron amorphous Boron powder (99.9% purity). These materials were lightly mixed in appropriate amounts and pressed into a pellet 10 mm thick and 20 mm in diameter. The pellets were placed on W foil, which was in turn placed between two W ingots. These whole assembly was burned at 1700 °C for two hours in an HV chamber at $2 \cdot 10^{-4}$ Pa by e-beam heating of W ingot. The TaB$_2$ samples were prepared in the same way from TaB$_2$ powder (Donezk Factory of Chemicals).

The resulting ceramic pellets had over 60–90% the theoretical mass density and were black in color. They demonstrated good metallic conductivity at low temperatures. After regrinding the prepared pellets in an agate mortar, the respective powders were placed in a tungsten can and melted by e-beam heating of the W crucible for a few minutes in HV chamber at $1 \cdot 10^{-4}$ Pa.

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Resulting melt had shiny single crystals about 0.1 mm in size on top with solid polycrystalline ingot underneath between melted W can walls. However, these single crystals were found to be nonsuperconducting due to presence of high concentration of W impurities observed from XRD. The MgB_2 samples were sintered from metallic Mg plates placed on top of Boron-pressed pellets. The pellets were placed on Mo foil, which was in turn placed on a Mo crucible. The crucible, with foil and pellets, was burned for two hours at 1400 °C in a tube furnace under an Ar pressure of 20 atm., with subsequent cooling to room temperature when furnace was turned off.
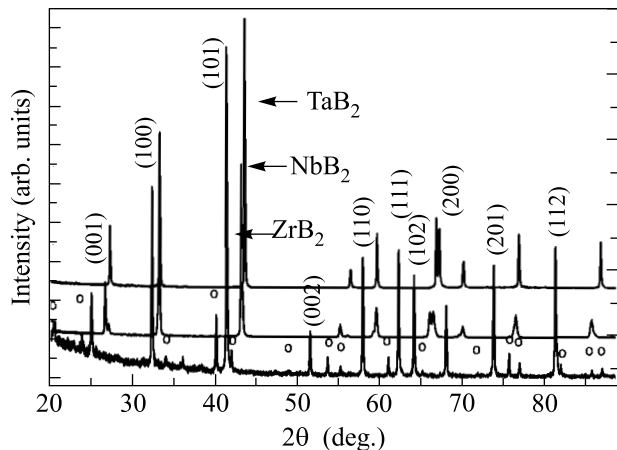

Fig.1 X-ray $\theta - 2\theta$ scan of ZrB_2, NbB_2, and TaB_2 pellets, at room temperature. The cycles mark the reflections from cubic ZrB_{12} ($a = 7.388$ Å) impurity

X-ray $\theta - 2\theta$ scan diffraction pattern (see Fig.1) was obtained using CuK_α radiation. The measurements showed the samples of all diborides to consist largely of the desired AlB_2 phase. We would like to note that a small amount of ZrB_{12} impurity phase was found to be present after first step of preparation. This phase was washed out after subsequent regrinding and annealing. The X-ray diffraction pattern was indexed within a hexagonal unit cell (space group $P6/mmm$). This crystal structure consists of honeycomb-net planes of Boron, separated by triangular planes of the metals. The analysis of the data yielded following values of the lattice parameters: $a = 3.170$ Å and $c = 3.532$ Å for ZrB_2, $a = 3.111$ Å, $c = 3.267$ Å for NbB_2, and $a = 3.087$ Å, $c = 3.247$ Å for TaB_2. All parameters are in good agreement with published data [11].

For resistive measurements we used following sample preparation procedure: the pellets were first cut by using a diamond saw with ethyl alcohol as coolant. Rectangular solid bars of about $0.5 \times 0.5 \times 6$ mm size were

obtained from pellets by using the spark erosion method. A standard four-probe ac (9 Hz) method was used for resistance measurements. Silver Print was used for making electrical contacts. The samples were mount in a liquid helium cryostat able to regulate the temperature from 1.8 K to room temperature. We employed a radio frequency (RF) coil technique for ac susceptibility measurement [12]. Magnetoresistivity measurements utilizing a superconducting magnet were also performed. A well-defined geometry of the samples allowed us to perform accurate measurements of resistivity with the magnetic field applied perpendicular to the direction of electric current.

Fig.2 shows the typical temperature dependence of the resistivity for ZrB_2 samples. The resistivity exhibits a very sharp superconducting transition at 5.5 K shown on Fig.2b. The transition width is about 0.14 K for a 10 to 90% drop. Such a narrow transition is a characteristic
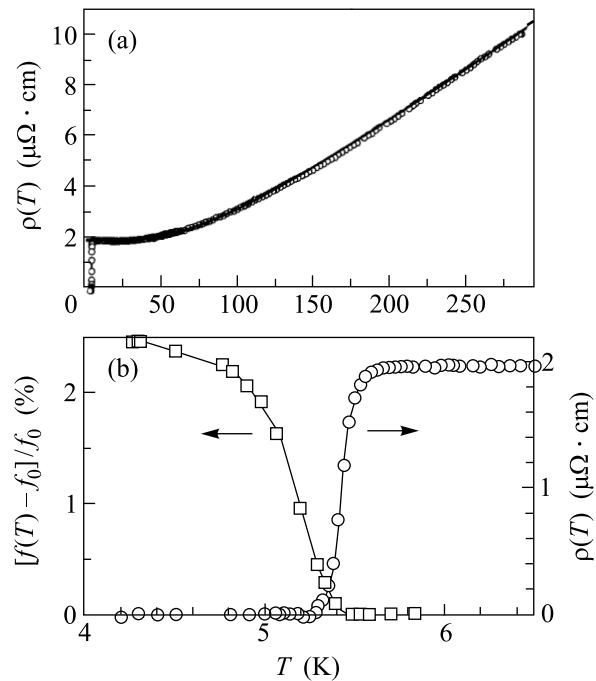

Fig.2. (a) Typical temperature dependence of the resistivity of ZrB_2 sample. Symbols denote the data and the solid line is Bloch-Grüneisen law fit with Debye temperature 280 K. (b) Low-temperature dependence of the ac susceptibility (proportional to the frequency shift $[f(T) - f_0]/f_0$- left axis) measured with the frequency $f_0 = f(6K) = 9$ MHz, and the resistivity (right axis) in ZrB_2

of good quality superconducting material. The resistivity value 10 $\mu\Omega \cdot$ cm at room temperature is almost the same as that of MgB_2 (see Fig.4), whereas the residual

resistivity is about $2\ \mu\Omega\cdot$ cm. One should note that the temperature dependence of the resistivity bellow $150\,$K, may be fitted by a square law, $\rho(T) = a + b \times T^2$, characteristic for electron-electron scattering [13]. Nevertheless, the overall temperature dependence of resistivity can be perfectly fitted with classical Bloch-Grüneisen law (solid line), with rather low Debye temperature, $T_D = 280\,$K.

Fig.2b shows temperature dependence of the normalized real part of ac susceptibility and the resistivity, $\rho(T)$, in the same ZrB_2 sample as on Fig.2a. For this type of measurements the sample is placed inside the inductance coil of LC circuit, and the resonant frequency of this circuit is monitored as a function of temperature. The temperature dependence of the sample ac susceptibility $\chi(T)$ causes changes in inductance L and in turn the resonant frequency $f(T)$ of the circuit, $\Delta f/f \propto -\mathrm{Re}\chi$. Susceptibility data of Fig.2a clearly show the superconducting transition in ZrB_2 sample at 5.5 K. The onset temperature of the ac susceptibility corresponds to the end point resistance transition, typical for superconducting transition.

Fig.3 shows magnetic field dependent electrical resistivity data taken at a variety of temperatures. Using these data, the resistive upper critical magnetic field, $H_{c2}(T)$, can be extracted from each curve. We can do it by extending the $\rho(H)$ line with maximum $d\rho/dH$ up to the normal state (see the dotted line). Fig.3b presents temperature dependence of the $H_{c2}(T)$ for a ZrB_2 sample derived from this extrapolation. Contrary to conventional theory [14], we found that the $H_{c2}(T)$ dependence is linear over an extended region of T with some downward curvature close to T_c. This leads to a rather low zero temperature value of $H_{c2}(0) = 0.1\,$T $(\xi(0) = 570\,\text{Å})$ which is significantly smaller than for MgB_2 (18 T) [15]. Such a linear $H_{c2}(T)$ dependence is characteristic for 2D superconductors [16] and was also observed in MgB_2 [15] wires and $BaNbO_{3-x}$ films [17, 18]. The results of extended study of the $H_{c2}(T)$ dependence ZrB_2 samples will be discussed elsewhere.

Fig.4 shows the temperature dependencies of the resistivity for NbB_2 and MgB_2 samples. Best fits were obtained using classical Bloch-Grüneisen law rather than $a + b \times T^2$ or $a + b \times T^3$ forms previously reported for MgB_2 [2, 3]. The solid fitting lines with the Bloch-Grüneisen form in Fig.4 nearly overlays the data. The Debye temperatures derived from these fits are rather high in comparison with ZrB_2, i.e. 460 K and 440 K for NbB_2 and MgB_2, respectively. The T_c value for the MgB_2 samples is the same that is found elsewhere, i.e. 39 K [1–3]. We suggest that previously reported T^2 and T^3 dependencies of the resistivity of MgB_2 may be due
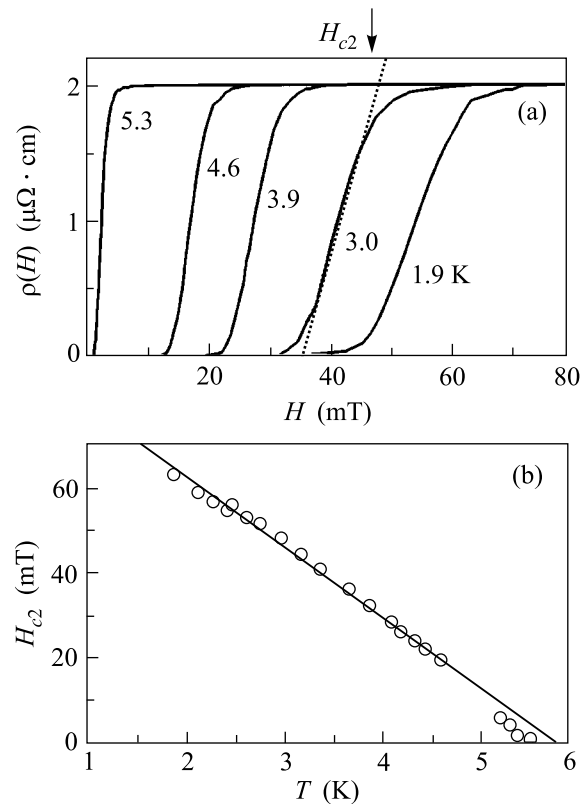

Fig.3. (a) Magnetic field resistive transition curves in ZrB_2 sample at different temperatures. The dashed line is drawn through the $\rho(H)$ dependence with maximal $d\rho/dH$ derivative for illustration of the H_{c2} determination. (b) Temperature variation of the upper resistive critical magnetic field $H_{c2}(T)$ in ZrB_2 sample

to rather high residual resistance, $\rho(0)$, of the samples and respectively weak $\rho(T)$ dependence. Our data are well consistent with the Bloch-Grüneisen law, which is characteristic for electron-phonon scattering [13]. Nevertheless, we believe that only data obtained on high purity single crystals can solidify this conclusion. Note that the resistivity ratio for all diborides studied is approximately 5 rather then 10000 or even few millions as for pure metals [13].

In contrast to the data of Ref. [9] our RF susceptibility measurements of TaB_2 samples did not reveal any superconducting transition. At the same time our XRD data have shown the same [9] clear AlB_2 spectra (see Fig.1). In contrast to [9], we did not find any impurities in our TaB_2 samples from XRD data (see Fig.1). Our resistive measurements up to $0.37\,K$ do not show any superconducting transition in NbB_2 as well. This contradicts the ac susceptibility data of Ref. [8], which reports the superconducting transition in NbB_2 to be at $0.62\,$K. We observed the superconducting transition at $4.4\,$K in
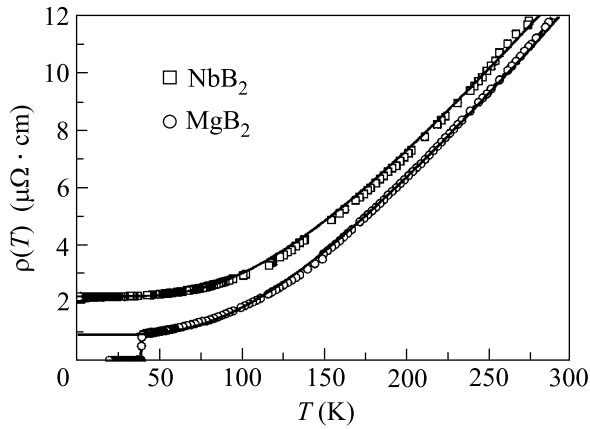
Fig.4. Typical temperature dependence of the resistivity of NbB_2 and MgB_2 samples. The solid lines denotes the Bloch-Grüneisen law fit with Debye temperatures 440 K and 460 K for MgB_2 and NbB_2, respectively

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melted TaB_2 samples while the XRD data of these samples revealed the presence of metallic Ta impurities. We believe these contradictions are due to the different sample preparation technique of Refs. [8, 9]. The samples used in those papers were prepared using a borothermic method from Nb_2O_5 and Ta_2O_5 pentoxides and *Boron* [19]. Therefore, those samples might consist of reduced Nb and Ta oxides intercalated by *Boron*, which could be the source of superconducting transition. Recently, we have shown that oxygen reduced $BaNbO_{3-x}$ compounds exhibit superconducting transition even at $T_c = 22$ K [17, 18]. Also, since the superconductivity in TaB_2 was not observed before on the samples made by the same technique [8], the reason of this discrepancy with data obtained in [9] should be emphasized from resistance measurements. Therefore, care must be taken for sample preparation and composition before final conclusions about superconductivity in NbB_2, TaB_2 as well in other diborides can be drawn.

In summary, we report the temperature dependence resistivity and high frequency susceptibility measurements of synthesized samples of ZrB_2, NbB_2, TaB_2 and MgB_2. We discovered a superconducting transition at 5.5 K in ZrB_2 samples. The superconducting transition width for the resistivity measurement was about 0.14 K, and the resistivity in the normal state followed a classical Bloch-Grüneisen behavior in all diborides studied. The linear $H_{c2}(T)$ dependence was observed for ZrB_2 samples over an almost full range of temperatures below T_c, leading to a rather low $H_{c2}(0) = 0.1$ T. Superconducting transition was not found in NbB_2 samples up to 0.37 K and TaB_2 samples above 4.4 K.