On Electron Transport in ZrB$_{12}$, ZrB$_2$ and MgB$_2$

V.A. Gasparov, M.P. Kulakov, N.S. Sidorov, and I.I. Zver’kova

Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russian Federation

V.B. Filipov, A.B. Lyashenko, and Yu.B. Paderno

Institute for Problems of Material Science NANU, Kiev, Ukraine

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We report on measurements of the temperature dependence of resistivity, $\rho(T)$, for single crystal samples of ZrB$_{12}$, ZrB$_2$ and polycrystalline samples of MgB$_2$. It is shown that cluster compound ZrB$_{12}$ behaves like a simple metal in the normal state, with a typical Bloch - Grüneisen $\rho(T)$ dependence. However, the resistive Debye temperature, $T_D = 300$ K, is three times smaller than $T_D$ obtained from specific heat data. We observe the $T^2$ term in $\rho(T)$ of these borides, which could be interpreted as an indication of strong electron-electron interaction. Although the $\rho(T)$ dependence of ZrB$_{12}$ reveals a sharp superconductive transition at $T_c = 6.0$ K, no superconductivity was observed for single crystal samples of ZrB$_2$ down to 1.3 K.

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It is known that boron has a tendency to form cluster compounds. In particular there are octahedral B$_6$ clusters in MeB$_6$, icosahedral B$_{12}$ clusters in $\beta$-rhombohedral boron, and cubo-octahedral B$_{12}$ clusters in MeB$_{12}$. So far, several superconducting cubic hexa - MeB$_6$ and dodecaborides - MeB$_{12}$ have been discovered (Me=Sc, Y, Zr, La, Lu, Th). Many other cluster borides (Me= Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm) were found to be ferromagnetic or antiferromagnetic. Even though the superconductivity in ZrB$_{12}$ was discovered a long time ago ($T_c = 6$ K), there has been little effort devoted to the study of electron transport and basic superconductive properties of dodecaborides. Only recently, the electron transport of solid solutions Zr$_{1-x}$Sc$_x$B$_{12}$ as well as the band structure calculations of ZrB$_{12}$ has been reported. Understanding the properties of the cluster borides as well as the superconductivity mechanism in these compounds is very important.

Recently, we reported superconductivity at 5.5 K in the polycrystalline samples of ZrB$_2$. This was not confirmed in later studies. It was recently suggested that this observation could be associated with nonstoichiometry in the zirconium sub-lattice. In this letter we address this problem. We present the results from measurement of the temperature dependencies of resistivity, $\rho(T)$, for single crystals of ZrB$_{12}$ and ZrB$_2$. Comparative data from polycrystalline samples of MgB$_2$ are also presented. The superconducting properties of ZrB$_{12}$ will be published elsewhere.

Under ambient conditions, dodecaboride ZrB$_{12}$ crystallizes in the fcc structure of the UB$_{12}$ type (space group $Fm\bar{3}m$), $a = 0.7408$ nm. In this structure, the Zr atoms are located at interstitial openings in the close-packed B$_{12}$ clusters. In contrast, ZrB$_2$ shows a phase consisting of two-dimensional graphite-like monolayers of boron atoms with a honeycomb lattice structure, intercalated with Zr monolayers (with lattice parameters $a = 0.30815$ nm and $c = 0.35191$ nm).

The ZrB$_2$ powder was produced by the boron carbide reduction of ZrO$_2$. The ZrB$_{12}$ single crystals were obtained from a mixture of a certain amount of ZrB$_2$ and an excess of boron (50 – 95%). The resulting materials were subjected to a crucible-free RF-heated zone-induction melting process in an argon atmosphere. The obtained single crystal ingots of ZrB$_{12}$ and ZrB$_2$ have a typical diameter of about 5 – 6 mm and a length of 40 mm. A metallographic investigation detected that the ZrB$_2$ crystal is surrounded by a polycrystalline rim about 0.5 mm thick. The measured specific density of the ZrB$_{12}$ rod is 3.60 g/cm$^3$, in good agreement with the theoretical density. The X-ray diffraction measurements confirmed that both ingots are single crystal. We found the cell parameters of ZrB$_{12}$, $a = 0.74072 \pm 0.00005$ nm, to be very close to the published values.

Polycrystalline MgB$_2$ and CaMgB$_2$ samples were sintered from metallic Mg or a mixture of Ca, Mg powders and boron pellets using a similar technique as outlined in our earlier work. This technique is based on the reactive liquid Mg,Ca infiltration of boron. X-ray diffraction patterns and optical investigation show large grains of single MgB$_2$ phase, with much smaller grains of semiconducting CaB$_6$ phase visible in-between. Density of MgB$_2$ grains was rather high, 2.4 g/cm$^3$, while the samples prepared from Mg infiltration had smaller density of 2.2 g/cm$^3$. Only MgB$_2$ samples cut from large grains were studied. These samples will be denoted as CaMgB$_2$.

We used a spark erosion method to cut the samples into a parallelepiped with dimensions of about 0.5 x 0.5 x 8 mm$^3$. Single crystal samples were oriented along [100] for ZrB$_{12}$, and in hexagonal [0001] and basal [1000] directions for ZrB$_2$, respectively. The orientation process was performed using an X-ray Laue camera.
samples were lapped by diamond paste and subsequently etched: ZrB$_{12}$ in hot nitrogen acid, ZrB$_2$ in mixture of H$_2$O$_2$/HNO$_3$/HF, and MgB$_2$ in 2%HCl plus water-free ethanol.

A standard four-probe ac (9Hz) method was used for resistance measurements. We used Epotek H20E silver epoxy for electrical contacts. The samples were mounted in a temperature variable liquid helium cryostat. Temperature measured by RF susceptibility and $\rho(T)$ was found to be $T_c\approx 5.97$ K for ZrB$_{12}$ samples and $39$ K for MgB$_2$ polycrystalline samples, respectively.

We display the temperature dependence of the resistivity for ZrB$_{12}$, MgB$_2$ and CaMgB$_2$ in Fig. 1 and that of ZrB$_2$ in Fig. 2. To emphasize the variation of $\rho(T)$ in a superconductive state, we plot these data in the inset of Fig. 1. The samples demonstrate a remarkably narrow superconducting transition with $\Delta T = 0.04$ K for ZrB$_{12}$ and with $\Delta T = 0.7$ K for both MgB$_2$ samples. Such a transition is a characteristic of good quality samples.

As we can see from Fig. 2 no superconductivity was observed in ZrB$_2$ down to 1.3 K, while a pronounced slope change in $\rho(T)$ is observed around 7 K. One can explain such behavior in the following way. In ZrB$_2$ the Fermi level is located in the pseudo gap. The presence of Zr defects in Zr$_{0.75}$B$_{2.25}$ leads to the appearance of a very intense peak in the density of states in the vicinity of the pseudo gap and subsequent superconductivity.

We strongly believe that the observation of was due to nonstoichiometry of our samples. Superconductivity in nonstoichiometric samples is very common in other borides: MoB$_{2.5}$, NbB$_{2.5}$, Mo$_2$B, W$_2$B, BeB$_{2.75}$.

It is worth noting that ZrB$_{12}$ is mostly boron, and one could speculate that its resistivity should be rather high. In contrast we observe that the room temperature resistivity of ZrB$_{12}$ is almost the same as for MgB$_2$ and ZrB$_2$ samples. The $\rho(T)$ is linear above 90 K with the slope of $\rho(T)$ more pronounced than in MgB$_2$ or ZrB$_2$. The residual resistivity ratio RRR of 9.3 for ZrB$_{12}$ as well as RRR $\approx 10$ for MgB$_2$ and ZrB$_2$ samples suggests that the samples are in the clean limit. One can predict a nearly isotropic resistivity for fcc ZrB$_{12}$, which can be described by the Bloch-Grüneisen (BG) expression of the electron-phonon e-p scattering rate:

$$\rho(t) - \rho(0) = 4\rho_1 t^5 \int_0^{1/t} \frac{x^5 e^x dx}{(e^x - 1)^2} = 4\rho_1 t^5 J_5(1/t)$$

Here, $\rho(0)$ is the residual resistivity, $\rho_1 = d\rho(T)/dT$ is a slope of $\rho(T)$ at high $T$, $T > T_R$, $t = T/T_R$, $T_R$ is the resistive Debye temperature and $J_5(1/t)$ is the Debye integral. As we can see from Fig. 1, all data for ZrB$_{12}$ fall very close to the theoretical BG function (solid line). To emphasize the variation of $\rho(T)$ at low $T$ we plot these data as $\rho(T) - \rho(0)$ versus $t^5 J_5(1/t)$ in Fig. 3 on a log-log scale. The BG formula predicts a linear dependence of $\log[\rho(T) - \rho(0)]$ versus $\log[t^5 J_5(1/t)]$ with the slope equal to unity. We use $T_R$ as a fitting parameter to achieve agreement at the high temperatures. For comparison, we also present our $\rho(T)$ data of ZrB$_2$ and MgB$_2$ calculated in a clean case of the two band model.

It is clear from Fig. 3 that above 25 K the BG model describes the $\rho(T)$ dependence of ZrB$_{12}$ fairly well. It is remarkable that this description works well with constant $T_R = 300$ K. At the same time, $T_D$ calculated from specific heat data is three times higher. Furthermore
summing Eq. (1) and Eq. (2), and living $K_T$ from on this discrepancy, we used a model applied to LaB$_6$ calculated in the two band model [12].

$T_D$ increases from 800 K to 1200 K as temperature varies from $T_c$ up to room temperature. In order to shed light on this discrepancy, we used a model applied to LaB$_6$ of Ref. 14. We can treat the boron sub-lattice as a Debye solid with $T_R$ and the Zr ions as independent Einstein oscillators with characteristic temperature $T_E$. The effect of the Einstein mode on the resistivity of a metallic solid is discussed in Ref. [12]:

$$\rho_E(T) = \frac{KN \cdot e^{T_E/T}}{M \cdot T (e^{T_E/T} - 1)^2}. \quad (2)$$

Here $N$ is the number of oscillators per unit volume, $K$ is a constant that depends on the electron density of the metal, $M$ is the atomic mass. We fit the data by summing Eq. (1) and Eq. (2), and living $KN/M$, $\rho_1$, $T_R$ as free parameters. Although the model calculations perfectly match the data (see solid line in Fig. 3), the $T_E$ we are getting is unreasonably small ($T_E = 50$ K), and the difference between $T_R$ and specific heat $T_D$ becomes even worse, $T_R = 270$ K. We believe that this in-consistency of $T_R$ and $T_D$ can be explained by limitation of $T_R$ by a cut-off phonon wave vector $q = k_BT/\hbar s$. The latter is limited by the Fermi surface (FS) diameter $2k_F$ [16] rather than the highest phonon frequency in the phonon spectrum.

According to band structure calculations [4], the FS of ZrB$_{12}$ consists of an open sheet along $\Gamma L$ direction at point $\Gamma$ with $k_{\Gamma X} = 0.47$ Å$^{-1}$, a quasi spherical sheet at point X ($k_{\Gamma X} = 0.37$ Å$^{-1}$) and a small sheet at point K ($k_{KT} = 0.14$ Å$^{-1}$). We suggest that $T_R$ is limited by the small FS sheet. Unfortunately the experimental FS model and the sound velocity are not yet known.

Therefore we cannot corroborate this suggestion by experimental FS.

As we can see from Fig. 3 the $\rho(T)$ of ZrB$_2$ and MgB$_2$ samples deviates from the BG model even more dramatically. Putti et al. [15] modified the BG equation introducing variable power $n$ for the $t^nJ_n(1/t)$ term in Eq. (1).

The best fit to the data was obtained with $n = 3$ which in fact ignores a small angle $e-p$ scattering. Recently Sollogubenko et al. [16] reported a cubic $T$ dependence in the $a,b$ plane resistivity below 130 K in the single crystals of MgB$_2$. This was attributed to the interband $e-p$ scattering in transition metals.

However, we believe there are strong objections to this modified BG model: (i) a cubic $\rho(T)$ dependence is a theoretical model for large angle $e-p$ scattering and no evidence of it was observed in transition and non-transition metals; (ii) the numerous studies of the $\rho(T)$ dependence in transition metals have been found to be consistent with a sum of electron-electron $e-e$, $T^2$, and $e-p$, $T^3$, contributions to the low $T$ resistivity, which may easily be confused with a $T^3$ law [11, 13, 20]; (iii) the interband $\sigma - \pi$ e-p scattering plays no role in normal transport in the two band model for MgB$_2$ [12].

In order to solve these problems, we added e-e scattering $T^2$ term in Eq. (1) [14, 20] as a possible scenario. Indeed, keeping in mind that the BG term is proportional to $T^5$ at $T < 0.1T_R$, $\rho(T)$ dependence may be presented in a simple way [19, 21]:

$$[\rho(T) - \rho(0)]/T^2 = \alpha + \beta T^3.$$  

Here $\alpha$ and $\beta = 497.6 \rho_1/T_R^2$ are parameters of $e-e$ and $e-p$ scattering terms, respectively. Such a plot should yield a straight line with slope of $\beta$ and its intercept with y-axis ($T = 0$) should equal to $\alpha$. Further, to be consistent with BG law, the $\beta$ parameter should lead to the same $T_D$ as obtained from high $T$ log-log fit in Fig. 3 and both coefficients must be independent of $\rho(0)$. We determined $\rho(0)$ from the intercept of linear $\rho(T)$ vs $T^2$ dependence with the $T = 0$ axis and plotted the $\rho(T) - \rho(0))/T^2$ vs. $T^3$ in Fig. 4. It is evident that the measured resistivity approaches a quadratic law at $T < 25$ K in ZrB$_2$, at $T < 100$ K in ZrB$_2$, and at $T < 150$ K in both MgB$_2$ samples.

The regime of applicability of two term fit is limited to temperatures below 0.1$T_R$. At larger $T$ the $e-p$ term increases more slowly than $T^5$ law and this is why the data are not consistent any more with the two terms equation. From the intercept with $T = 0$ axis, we find very similar values of $\alpha$ for ZrB$_{12}$ and ZrB$_2$ samples in the basal plane ($\alpha = 22.9 \rho\Omega cmK^{-2}$ and $15.9 \rho\Omega cmK^{-2}$, respectively) while $\alpha$ is about five times larger for CaMgB$_2$ sample, 95 $\rho\Omega cmK^{-2}$. The slopes of $\beta$ give $\rho_1$ and $T_R$ values largely consistent with high temperature log-log fits for the ZrB$_{12}$ and ZrB$_2$ samples.

However, low $T$ results for $\beta$ and $\rho_1$ are far from consistent with high $T$ data for both MgB$_2$ and CaMgB$_2$ samples. Nevertheless, the magnitude of $T_R = 900$ K for MgB$_2$ extracted from log-log fit above 150 K, is in excellent agreement with $T_D = 920$ K obtained from low-temperature specific heat measurements [21], and is
considerably lower than the reported data based on \( T^3 \) dependence of \( \rho(T) \) \((T_R = 1050 \sim 1226 \, K) \), where \( T^2 \) term was ignored. \(^{4, 17, 13}\). A similar fit for theoretical curve is even more consistent with \( T_R = 900 \, K \), however we have to mention that violation of Matthiessen’s rule in MgB\(_2\) may mask the intrinsic \( \rho(T) \) dependence \(^{12}\).

In general, there are many scattering processes responsible for the \( T^2 \) term in \( \rho(T) \) of metals: (i) size, surface, dislocation and impurity scattering induced deviations from Matthiessen’s rule (see references in \(^{22}\)); (ii) \( e-p \) scattering for small cylindrical FS sheets relative to the phonon wave vector \(^{10}\); (iii) inelastic electron impurity scattering \(^{21}\); (iv) the quantum interference between \( e-i \) and \( e-p \) scattering \(^{19}\); (v) \( e-e \) scattering \(^{19, 21}\).

We can estimate some of these effects. We use Drude law to obtain the residual electron mean free path \( l = \frac{4\pi e\nu_F}{\sigma} \). Using a Fermi velocity of \( v_F = 3.2 \cdot 10^7 \, cm/s \) and a plasma frequency \( \omega_p = 5.16 \cdot 10^{15} \, s^{-1} \) for MgB\(_2\) \( \sigma\)-band \(^{12}\), we obtain \( l \approx 100 \, nm \). This implies that size effects are negligible for both MgB\(_2\) samples and Zr borides. In agreement with ZrB\(_2\) data (see Fig. \(^1\) the \( \alpha \) is proportional to \( \rho(0) \) for inelastic \( e-i \) scattering \(^{23, 24}\). However, this term is 1.5 times lower for CaMgB\(_2\) relative to MgB\(_2\), which has the same \( \rho(0) \).

We can try to estimate contribution from the small FS sheets to \( \alpha \). The \( T^2 \) term was observed in \( \rho(T) \) and electron scattering rates of Bi and Sb, which was attributed to a missing of one \( q \) component for \( e-p \) scattering on small cylindrical FS sheets \(^{16}\). The FS of MgB\(_2\) is composed of two warped open cylinders running along the \( c \) axis, which arise from \( \sigma \) boron orbitals \(^{12, 27}\). The FS of ZrB\(_2\) consist of nearly ellipsoidal surfaces joined together at the corners \(^{26, 27}\), which may also be responsible for the \( T^2 \) term in \( \rho(T) \). We can use the sound velocity \( s = 1.1 \cdot 10^9 \, cm/s \) and \( 8 \cdot 10^5 \, cm/s \) for MgB\(_2\) and ZrB\(_2\), respectively \(^{28, 29}\), to estimate the lowest temperature, \( T_{\text{min}} = \frac{\hbar k_F}{\sigma s} \), when the phonon wave vector \( q \) matches a neck of smaller \( \sigma \) tube in MgB\(_2\) \( (k_\sigma = 0.129 \, \AA^{-1}) \) or a diameter of the ellipsoidal sheets in ZrB\(_2\) \( (k_F = 0.095 \, \AA^{-1}) \). We obtain \( T_{\text{min}} = 95 \, K \) and 60 \( K \), respectively. Thus we conclude that \( q < k_F \) at \( T < 100 \, K \) in both diborides, which implies that the contribution of the 2D FS sheets to \( \alpha \) is negligible.

In general only umklapp \( e-e \) scattering contributes to \( \rho(T) \), whereas the normal collisions are significant in compensated metals and in thermal resistivity \(^{20}\). Borides have rather high \( T_D \) which depresses the \( e-p \) scattering, so that the \( e-e \) SR term is easier to observe. Notice however that the \( \alpha \) value for MgB\(_2\) is five times larger than corresponding values in ZrB\(_{12}\) and ZrB\(_2\). The latter values are in turn five times larger than in transition metals \( (\alpha_{\text{MgB}} = 2.5 \frac{\rho\Omega}{cm/K^2} \) and \( \alpha_{\text{W}} = 1.5 \sim 4 \frac{\rho\Omega}{cm/K^2} \)) \(^{19, 20}\). Therefore, additional experiments must be performed for more pure samples before final conclusion about the origin of the \( T^2 \) term in borides can be drawn.

In conclusion, we present a study of the \( \rho(T) \) of single crystals of ZrB\(_{12}\), ZrB\(_2\) and polycrystalline samples of MgB\(_2\). Large differences between resistive and specific heat Debye temperatures have been observed for ZrB\(_{12}\). The results provide evidence of a \( T^2 \) term for all these borides at low \( T \), whose origin is not yet understood.

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