Tunneling and magnetic characteristics of superconducting ZrB_{12} single crystals

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(Received 2 February 2004; published 24 June 2004)

Bulk and surface properties of high-quality single crystals of zirconium dodecaboride have been studied in the temperature range from 4.5 K up to the superconducting transition temperature, which is found to be nearly 6.06 K. Scanning tunneling spectroscopy data, together with dc and ac magnetization measurements, are consistent with the conventional *s*-wave pairing scenario, whereas they disagree in estimates of the electron-phonon coupling strength. We explain the divergence, supposing a great difference between the surface and bulk superconducting characteristics of the compound. This assertion is supported by our findings of a nonlinear magnetic response to an amplitude-modulated alternating magnetic field, testifying to the presence of surface superconductivity in the ZrB_{12} samples at dc fields exceeding the thermodynamic critical field.

DOI: 10.1103/PhysRevB.69.212508 PACS number(s): 74.70.Ad, 74.25.Op, 74.50.+r, 74.25.Ha

Owing to the unique combination of physical properties such as high melting point, hardness, and thermal and chemical stability, metal-boron compounds have found different applications.[1,2] The discovery[3] of superconductivity in metallic MgB_2 at the unexpected T_c of 39 K has caused great interest in other transition-metal diborides that show lower T_c values. Related experimental efforts have recently been extended to a wider class of binary boron-containing intermetallic compounds, in particular, to zirconium dodecaboride.[4,5]

Measurements on polycrystalline ZrB_{12} (as well as on many other boron-rich compounds) were done by Matthias *et al.*[6] where $T_c = 5.82$ K was determined from the sharp transition in specific heat data. (Our estimate for T_c detected by dc magnetization measurements agrees with the value[7] of $T_c \approx 6.0$ K). Despite assertions that the ZrB_{12} phase exists only at high temperatures,[8] large high-quality single crystals of ZrB_{12} were grown in Kiev[9] and by Leithe-Jasper *et al.*[10] Whereas this work[10] reported only crystallographic data for the crystals, two groups[4,5] have performed investigations of ZrB_{12} single crystals grown in Kiev[9] by different physical methods. Some unexpected results have been derived, and different conclusions relating to the nature of superconductivity in this compound were claimed. Gasparov *et al.*[4] observed a linear temperature dependence of the magnetic field penetration depth below 3 K, which contradicts the standard BCS theory, and proposed a *d*-wave-like pairing in ZrB_{12}. On the other hand, Daghero *et al.*,[5] based on resistivity versus temperature data and the well-known McMillan formula for T_c, concluded that ZrB_{12} is a conventional *s*-wave superconductor with a zero-temperature energy-gap value $\Delta(0) = 0.97$ meV and the ratio $2\Delta(0)/T_c = 3.64$. The same authors[5] have also measured point-contact conductance spectra that were found to be dominated by features typical of an *s*-wave superconductor but with the value $\Delta(T) = 0.97$ meV at T nearly 4 K [the BCS model yields $2\Delta(0)/T_c = 4.8$]. The only issue that the two groups[4,5] agree on is that the single crystals studied are type-II superconductors with an upper critical field $H_{c2}(0)$ above 1000 Oe, as estimated in Ref. 4 from resistance measurements, and in Ref. 5 as the field in which the Andreev-reflection features in conductance characteristics disappear.

In this work, we have studied tunneling and magnetic characteristics of ZrB_{12} single crystals grown in Kiev. The measurements were performed for temperatures ranging from above T_c down to 4.2 K, where analytical expressions obtained within the standard Ginzburg-Landau approximation[11] may be applied. In the following, we address two issues: the pairing symmetry in ZrB_{12} single crystals and whether they are really type-II superconductors. We have also studied surface characteristics with linear and nonlinear ac magnetic response measurements. Chemically, dodecaborides are the extremely stable materials in comparison with other borides and are characterized by a strong surface resistance to mechanical and chemical factors.[12] The difference between surface and bulk properties is discussed.

Large rods of ZrB_{12} single crystals were grown by the Kiev group with typical dimensions of about 6 mm in diameter and up to 40 mm in length. A $10.3 \times 3.2 \times 1.2$ mm^3 rectangular sample was cut from the rod and was polished mechanically by diamond and chemically etched in a boiling HNO_3/H_2O 1:1 mixture for 10 min to remove the Beibly layer. Room-temperature x-ray diffraction measurements performed in Kiev and in Jerusalem confirmed that the ZrB_{12} sample is a single-phase material with a UB_{12} structure [the space group of $Fm3m$, $a = 7.407$ Å (Ref. 13)].

The order parameter symmetry of ZrB_{12} was studied by scanning tunneling spectroscopy measurements of current-voltage (I-V) curves. In contrast to the point-contact technique,[5] the differential conductance dI/dV vs V yields direct information on the local quasiparticle density of states, and hence on the superconductor gap symmetry. The samples

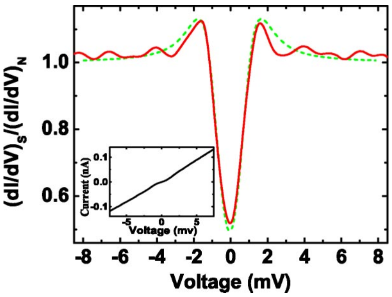

FIG. 1. (Color online) Representative tunneling spectrum of ZrB_{12} at T nearly 4.2 K (solid line) together with its fit to the temperature-smeared Dynes formula (see text) shown by a dashed line, with fitting parameters $\Delta(T)=0.97$ meV and $\Gamma=0.15$ meV. The inset shows the initial current-voltage characteristic.

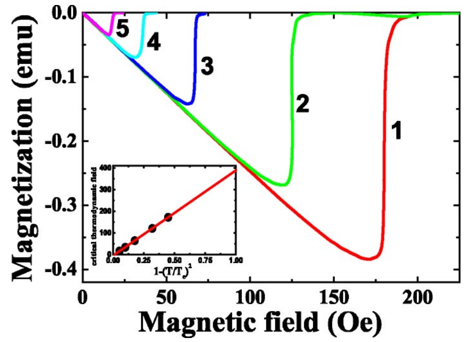

FIG. 2. (Color online) Magnetic field dependence of the magnetic moment at various temperatures: 1–4.5 K, 2–5.0 K, 3–5.5 K, 4–5.75 K, 5–5.9 K. The solid line in the inset is an extrapolation of the thermodynamic critical field behavior (2) deduced from the calculated $H_c(T)$ shown by circles.

were carefully cleaned with ethanol in an ultrasonic bath just before they were mounted into our cryogenic homemade scanning tunneling microscope.[14] Before inserting He exchange gas (through a trap) the sample space was evacuated and the device was dipped into a liquid-helium storage Dewar. After a sufficiently long thermalization period the sample temperature was somewhat above 4.2 K, but lower than 4.4 K, as was indicated by a sensor placed nearby. Tunneling measurements were performed for junction normal-state resistances between 50 and 500 MΩ. I-V characteristics were differentiated numerically in order to obtain normalized spectra $(dI/dV)_S/(dI/dV)_N$, the ratios of differential conductances in superconducting and normal states. The spectra were compared with a temperature-smeared[15] version of the Dynes formula[16] that takes into account the effect of incoherent scattering events inside a superconductor, by introducing a damping parameter Γ into the conventional s-wave BCS expression for a normalized quasiparticle density of states $N(\varepsilon)=\mathrm{Re}[(\varepsilon-i\Gamma)/\sqrt{(\varepsilon-i\Gamma)^2-\Delta(T)^2}]$.

The well reproducible local tunneling characteristics (Fig. 1) did not change significantly with the tip position and/or the device settings. All curves demonstrated coherence peaks with a pronounced minimum at $V=0$ and a near-gap structure symmetrical with respect to the bias voltage V. Gap values $\Delta(T\approx 4.2\text{ K})$ were found to be 0.97 ± 0.01 meV (which coincides well with point-contact findings[5] for the same temperature) with Γ not exceeding 0.15 meV. A relatively small value of the damping factor (in particular, compared with those in Ref. 5) is believed to prove the high quality of the sample surface. For all tip positions we have not observed any signs of a zero-bias peak known as a fingerprint of the d-wave pairing[17] and, hence, may reject the assumption about an unusual symmetry of the order parameter in ZrB_{12}.

The latter statement was also confirmed by zero-field-cooling dc magnetization M-vs-H measurements performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with external magnetic fields aligned parallel to the long axis of the sample. In the normal state (above 6 K) the dc susceptibility $\chi_{dc}=M/H$ is diamagnetic as expected.[7] Figure 2 shows the magnetization curves measured at various temperatures, corrected by the demagnetization factor N. Usually, when the external field is parallel to the long axis of a parallelepiped, N is small (the reduction in the H is a few percent) and can be neglected. However, for a sharp transition (as in our case) its width is of the same order as this reduction and more detailed analysis is needed. Using the expressions for an ellipsoid[18] and interpolating between the extreme cases that correspond to two different transverse sizes, $N=0.06$ was chosen. After this correction, the nearly vertical magnetization curves were obtained as shown in Fig. 2. This vertical shape close to the critical field values and the tiny hysteresis loops observed (not shown in Fig. 2) lead to the conclusion that bulk ZrB_{12} is a type-I superconductor or, alternatively, a type-II superconductor in which the Ginzburg-Landau parameter κ is slightly above the marginal value of $\kappa=0.71$.[11]

From the data presented in Fig. 2 we can estimate the thermodynamic critical fields H_c, whose equivalent magnetic energy is equal to the area under the measured M-vs-H dependence $\int_0^\infty[-M(H)]dH=H_c^2/(8\pi)$. According to the standard BCS theory for an s-wave superconductor, the critical field curve $H_c(T)$ should saturate at low temperatures and be linear in the vicinity of $T=T_c$:[11]

$$H_c(T) = 1.735 H_c(0)(1 - T/T_c). \tag{1}$$

The latter analytical result allows us to prove the conventional symmetry of the pairing in ZrB_{12} and to determine its T_c value. Experimental data shown in Fig. 2 agreed very well with the linear dependence (1) (the derivative $[dH_c(T)/dT]_{T=T_c}$ was equal to -110 Oe/K) and an extrapolation of $H_c(T)$ to zero yielded $T_c=6.06$ K. Now it is possible to use the empirical formula

$$H_c(T) = H_c(0)[1 - (T/T_c)^2], \tag{2}$$

which interpolates the overall behavior of $H_c(T)$ between $T=0$ and $T=T_c$, to estimate the zero-temperature thermodynamic critical field. Figure 2 (inset) yields $H_c(0)$ as 390 Oe. Using the density of states at the Fermi energy calculated recently for ZrB_{12} by Shein and Ivanovskii[19] $N(\varepsilon_F)=1.687$ 1/(eV cell) and the bulk energy-gap value of 0.97 meV from Ref. 5, one can estimate the condensation energy within the BCS theory and to evaluate the thermodynamic critical field

$H_c(0)$. The value obtained is nearly 300 Oe, which compares reasonably well with our estimation of $H_c(0)$ listed above. Again, we see no reason to suppose any deviation from the conventional gap symmetry and the phonon origin of the Cooper pairing in ZrB_{12}.

More problematic is the question about the electron-phonon coupling strength. As was pointed out by Rammer,[20] the ratio $H_c(0)/(T_c|dH_c/dT|_{T=T_c})$ can serve as its indicator. In the weak-coupling limit it equals 0.58, as follows from Eq. (1), whereas strong-coupling effects lead to a significant reduction of this quantity.[20] In our case, this ratio equals to 0.59 which, together with the conclusions of the resistivity measurements[5] places ZrB_{12} into the category of weak-coupling superconductors. At the same time, using the temperature dependence of the BCS energy gap[11] and our value for the energy gap at $T\approx 4.2$ K, we obtain $\Delta(0) = 1.21-1.24$ meV in excellent agreement with $\Delta(0) = 1.22$ meV extrapolated in Ref. 5 from point-contact measurements. In this case the ratio $2\Delta(0)/T_c$, the characteristic of the electron-phonon coupling strength,[21] equals 4.75 ± 0.10, indicating clearly an extremely strong electron-phonon interaction. According to Ref. 21, there is a general trend of the $2\Delta(0)/T_c$ growth with increasing T_c/ω_{ln} (ω_{ln} is a characteristic energy of lattice vibrations) and for $2\Delta(0)/T_c = 4.75$, ω_{ln} should be as great as 0.15.[21] The presence of such low phonon energies is doubtful, and, to explain this result, we assume that the order parameter is higher near the sample surface. In particular, it should lead[22] to a surface nucleation fields H_{c3} larger than those expected for a uniform sample.

To study the superconducting sheath state in the field range $H_c < H < H_{c3}$, we applied an additional small ac magnetic field $h(t)$ upon the coaxial dc field H and detected the linear and nonlinear responses.[23] The measurements have been done with our original homemade setup[24] adapted to the MPMS SQUID magnetometer. In linear experiments the ac field $h(t)=h_0 \cos \Omega t$ with $0<h_0<0.4$ Oe and $\Omega/2\pi = 1455$ Hz was generated by a copper solenoid inside the magnetometer and the ac susceptibility versus H was measured by the two-coil method. To study nonlinear characteristics of the sample, the ac perturbation had the form of an amplitude-modulated ac field $h(t)=h_0(1+\alpha \cos \Omega t)\cos \omega t$ with two additional parameters $\alpha\approx 0.9$ and $\omega/2\pi = 3.2$ MHz (see for details Ref. 24, where the same technique was applied to a Nb single crystal) and the amplitude of a rectified signal at the modulation frequency A_Ω was measured as a function of the dc field H.

Figure 3(a) exhibits a gradual shift of the real part χ' of the ac susceptibility compared with χ_{dc} calculated from dc magnetization curves. Such behavior was explained in Ref. 23 as an impact of the surface superconductivity that appears in perfect samples in a dc field parallel to the sample surface and persists in a surface region adjacent to a vacuum interface up to a field H_{c3}. Near T_c H_{c3} is defined by a simple relation $H_{c3}=2.38\kappa H_c$.[11] The shift between ac and dc susceptibility curves strongly depends on the amplitude and frequency of the ac field $h(t)$ and, because of that, any interpretation and determination of a critical field value H_c based on ac techniques should be done carefully. The nonlinear response A_Ω was detected only above H_c [Fig. 3(b)] where χ_{dc} vanishes, and hence the sample bulk was in a normal state. It corresponds to the direct observations[23] of a nonlinear nature of the response wavefront when a sinusoidal ac field is applied to a specimen in a superconducting sheath state. Variations of h_0 cause identical behavior of A_Ω in a Nb single crystal[24] where the presence of surface superconductivity was proven by different authors (see, for example, Ref. 25). In our case, the ratio H_{c3}/H_c near T_c is about 1.8. For a vacuum interface, the Ginzburg-Landau parameter should exceed the marginal value of $\kappa=0.71$, which divides type-I and type-II superconductors. But if the order parameter increases near the interface (as it is argued above), then the ratio of the surface nucleation field H_{c3} to the thermodynamic critical field can be dramatically enhanced (see Fig. 1 in Ref. 22). Then our data could be interpreted with an assumption of type-I superconductivity. Additional experiments are needed to define the value of the Ginzburg-Landau parameter in ZrB_{12} single crystals.

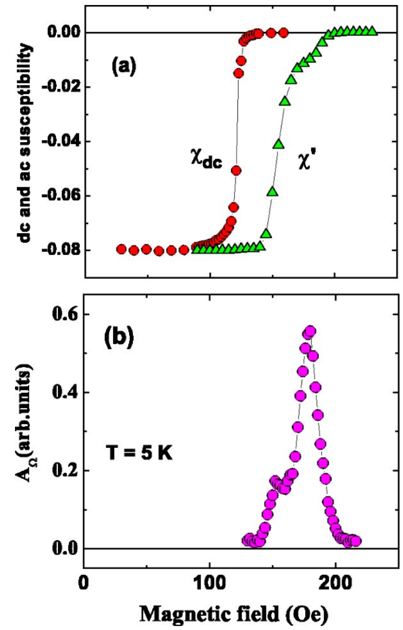

FIG. 3. (Color online) Magnetic field dependence of the dc susceptibility χ_{dc} compared with the real part of the ac susceptibility χ' at the fundamental frequency Ω (a) and of the rectified signal amplitude A_Ω (b); $T=5.0$ K.

In conclusion, we have proven experimentally that ZrB_{12} single crystals are conventional *s*-wave superconductors with enhanced surface characteristics. The latter statement can principally explain the difference in estimations of the electron-phonon coupling strength and of critical magnetic fields between the three studies performed on the same single crystals. More investigations are needed to explain all findings in this nontrivial material, in particular, the absence of the field direction effect reported in Ref. 5 (note that surface superconductivity should be strongly suppressed when the magnetic field has a component normal to the surface). We believe that zirconium dodecarboride is an interesting and fruitful compound for future experiments because of three reasons. First, due to excellent surface properties it can serve as a very suitable model material for studying specific near-surface superconducting properties that are not yet well understood.[25] Second, our experiments show that it is an unusual marginal superconductor near the border between type-I and type-II superconductors. And last, ZrB_{12} (similar to other dodecaborides) rises above conventional materials due to its outstanding resistance to external mechanical and chemical factors. We believe that its unique material properties and comparatively simple superconducting characteristics will attract the attention of the applied physics community to the compound, which can find its place among various superconducting bulk applications where strong abrasion- and chemical-resistant properties are required.

We are thankful to R. S. Gonnelli, I. R. Shein, and J. Kötzler for valuable discussions. This work was supported by the INTAS program under Project No. 2001-0617.

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