Doping-induced superconductivity of ZrB$_2$ and HfB$_2$

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Unlike the widely studied s-type two-gap superconductor MgB$_2$, the chemically similar compounds ZrB$_2$ and HfB$_2$ do not superconduct above 1 K. Yet it has been shown that small amounts of self or extrinsic doping (in particular with vanadium), can induce superconductivity in these materials. Based on results of different macroscopic and microscopic measurements, including magnetometry, nuclear magnetic resonance (NMR), resistivity, and muon-spin rotation ($\mu$+SR), we present a comparative study of Zr$_{0.96}$V$_{0.04}$B$_2$ and Hf$_{0.97}$V$_{0.03}$B$_2$. Their key magnetic and superconducting features are determined and the results are considered within the theoretical framework of multiband superconductivity proposed for MgB$_2$. Detailed Fermi surface (FS) and electronic structure calculations reveal the difference between MgB$_2$ and transition-metal diborides.

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I. INTRODUCTION

Borides, carbides, and nitrides were among the early compound superconductors discovered in the first half of the previous century [1] (see, e.g., Ref. [2] for a recent review). However, it was only in 2001, with the discovery of superconductivity in MgB$_2$ at 39 K [3], that researchers intensified the search for superconductivity in other diborides. Based on a large number of studies, MgB$_2$ was identified as a two-band two-gap superconductor. Its peculiar Fermi surface exhibits two-dimensional hole-like cylinders from the $p_{x,y}$ bands, a hole-like tubular network due to the bonding $p_z$ bands, and an electron-like tubular network due to the antibonding $p_z$ bands [4]. Due to this electronic configuration and to a distinct anisotropy of the electron-phonon interaction strength, the electronic excitation spectrum of MgB$_2$ adopts two gaps in the superconducting phase: a large gap of 7.2 meV in the $p_{x,y}$ ($\sigma$) bands, and a small gap of 2.8 meV in the bonding and antibonding $p_z$ ($\pi$) bands. At the same time, an upper critical field anisotropy has been observed, with $\mu_0 H_{c2}^{\perp} \sim 30$ T and $\mu_0 H_{c2}^{\parallel} \sim 3$ T at zero temperature [5].

Besides alkaline-earth metals (such as Mg), diborides of other elements have been proposed to be checked for superconductivity. Because of the presence of partially filled 3$d$, 4$d$, and 5$d$ orbitals, considered as promising for superconductivity, these new attempts involved isoagens (Al) and various $d$-type transition metals (T). The second of these (TB$_2$), which are claimed to combine average coupling constants with comparable phonon frequencies to MgB$_2$ [6] (due to the presence of light boron atoms), were the natural candidates in this search. Unfortunately, these renewed efforts proved unsuccessful and to date there are no reports of superconductivity for the majority of TB$_2$ materials.

ZrB$_2$ and HfB$_2$ are two such nonsuperconducting refractory materials with melting points of $\sim$3000 K, behaving essentially as Pauli paramagnets down to low temperatures. The electrons in the 4$d$ shell of zirconium (Zr) and those in the 5$d$ shell of hafnium (Hf) are less localized than those of the 3$d$ row. In a recent study [7] it was found that by replacing small amounts of Zr or Hf with V, the resulting compounds Zr$_{0.96}$V$_{0.04}$B$_2$ and Hf$_{0.97}$V$_{0.03}$B$_2$ are superconductors. Maximum superconducting temperatures $T_c = 8.33$ K and 7.31 K were reached in Zr$_{0.96}$V$_{0.04}$B$_2$ and Hf$_{0.97}$V$_{0.03}$B$_2$, respectively, at the upper solubility limit of V ($x \approx 0.04$). X-ray powder diffraction (XRD) patterns [7] indicate that an increase in V doping does not change the in-plane lattice parameter $a$, while it reduces the interlayer distance $c$. At the same time, it has been shown that the structural and electronic properties of these compounds are influenced by the presence of B vacancies [8].

In Ref. [7], the properties of superconducting Zr$_{0.96}$V$_{0.04}$B$_2$ were investigated by means of macroscopic techniques [7]. In this work we aimed at combining macroscopic and microscopic techniques (including magnetometry, NMR, resistivity, and preliminary $\mu$+SR experiments) on Zr-based diborides and extend our study to include the Hf-based compound. Since we succeeded in synthesizing samples with less magnetic impurities (below 10 ppm) with respect to the previous ones [7], whenever relevant, a comparison between the two batches is included. Our extensive data sets allowed us to unravel clear analogies and differences between the T-diborides Zr$_{0.96}$V$_{0.04}$B$_2$ and Hf$_{0.97}$V$_{0.03}$B$_2$ and the well-known MgB$_2$. In Sec. IV A we show that spin-lattice relaxation processes in T-diborides are two orders of magnitude slower that in MgB$_2$, indicating significantly different electronic structures. Combined magnetometry (Sec. IV B) and resistivity (Sec. IV C) measurements were performed to evaluate the upper and lower critical fields, respectively. These compounds prove to be extreme type-II superconductors, as reflected by the high values ($\sim$100) of the Ginzburg-Landau $\kappa = \lambda/\xi$ parameter. The London penetration depth $\lambda$ was evaluated through $\mu$+SR (Sec. IV D) experiments and the coherence length $\xi$ via upper critical field measurements (Sec. IV C). Thanks to the complementarity of the used techniques, we argue that, besides the qualitatively different Fermi surfaces of MgB$_2$ and transition-metal diborides, in both cases we are dealing with s-wave superconductors. While the rather high $T_c$ of MgB$_2$ is understood as a consequence of a favorable electronic structure.

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and electron-phonon interaction, the drastic effect of V-doping in the T-diborides is still rather surprising.

II. ELECTRONIC STRUCTURES OF ZrB2 AND HfB2

Both pure and V-doped compounds crystallize in the layered AlB2 structure with a $P6/mmm$ hexagonal space group, where the Zr (or Hf) atoms and the B atoms occupy, respectively, the $1a (0,0,0)$ and $2d (1/3, 2/3, 1/2)$ positions. As in MgB2, their crystal lattices are characterized by hexagonal metal layers alternating with graphite-like B layers (see Fig. 1).

Previous results of band-structure calculations [9,10] and Fermi surface (FS) representations [9] are available in the literature for both ZrB2 and HfB2. Since, however, the Fermi surface (FS) representations [9] are available in the literature for both ZrB2 and HfB2. Since, however, the Fermi surface (FS) representations [9] are available in the literature for both ZrB2 and HfB2. Since, however, the Fermi surface (FS) representations [9] are available in the literature for both ZrB2 and HfB2.

Polycrystals of ZrB2, HfB2, Zr0.96V0.04B2, and Hf0.97V0.03B2 were synthesized via boron carbide reduction and structurally characterized as described in Ref. [7]. The ZrB2 FS consists of four short cylindrical hole-type pockets around the $A$ point and four tripod-shaped electron-type pockets, each consisting of a triangular ring around the $K$ point and three elliptic extensions near the $\Gamma'AH$ plane. Since the FS of HfB2 exhibits essentially the same features, we refrained from presenting it in a separate figure. These features are quite different from those of the FS of MgB2. Most obvious is the reduction of the two almost two-dimensional hole sheets centered near the $A$ point for MgB2 to one much smaller and three-dimensional (3D) type pocket for Zr- and Hf-diboride. Likewise the 3D parts are quite different in shape for MgB2.

The FS plot was generated using the XCrySDen program [17] based on the DMol$^3$ output for a $99 \times 99 \times 99$ $k$ mesh.

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Preliminary $\mu^+\mathrm{SR}$ measurements were made at the GPS spectrometer of the $\mu$S facility of Paul Scherrer Institute (PSI) in Villigen, Switzerland. The available sample mass (300 mg) was sufficient to stop the 4-MeV muons without additional degraders and with a minimal background signal. To avoid pinning effects, well known for distorting the vortex lattice (VL) in the superconducting phase of MgB$_2$ [18], the transverse-field (TF) muon-spin rotation measurements were made at the highest field available (0.6 T).

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Nuclear magnetic resonance

The $^{11}$B NMR lines of all the samples (both pure and V-doped) were measured from 5 to 295 K; typical data are shown in Fig. 3. The reference $^{11}$B NMR frequency in an applied magnetic field of 3.505 T was evaluated to be $\nu_0 \approx 47.8844$ MHz. In our case, the NMR lines exhibit peaks which are very close to the reference, with an absolute positive shift of only about 6 kHz, corresponding to a Knight shift of 120 ppm. In the covered temperature range between 5 and 295 K the $^{11}$B NMR lines practically coincide (see Fig. 3), implying temperature-independent Knight shifts for all the measured samples, compatible with the $\chi(T)$ plateaux observed in the magnetometry data, measured under zero-field cooled conditions (see Fig. 4). The trend of the Knight shift in the superconducting phase could not be resolved because of the appreciable width of the resonance signal. As the line position, also the full width at half maximum (FWHM) is practically constant upon varying the temperature. For the Zr-based samples its value is 13 kHz (with 1 kHz of additional broadening below $T_c$), while for those containing Hf the width is 14 kHz (+1 kHz at low temperatures). The typical quadrupole splitting $\nu_Q$ in ZrB$_2$ and HfB$_2$ is approximately the same, i.e., 54 kHz. This relatively small value implies a rather small electric-field gradient (EFG), especially if compared with MgB$_2$, for which $\nu_Q \approx 860$ kHz [19], which is a signature of a different electronic charge distribution, confirmed by the different orbitals involved in the bonds, i.e., only $s$ and $p$ orbitals for MgB$_2$ and also $d$ orbitals for T-borides.

For typical powder spectra of a $I = \frac{3}{2}$ nucleus with a small quadrupole splitting, an analytical expression for the lineshape can be derived by considering the quadrupole term as a first-order perturbation in the main Zeeman Hamiltonian [20,21]. As shown in Fig. 3, the experimental spectrum and the simulated lineshape (dashed line) for ZrB$_2$ agree quite well. The simulation of the powder spectrum, employing a Gaussian broadening function [22,23]. From a quantitative analysis, the electric-field gradient (EFG) tensor can be evaluated using

$$eq = \frac{2I(2I-1)\hbar\nu_Q}{3eQ},$$  

with $eq$ the largest EFG component (parallel to the applied magnetic field), $I$ the nuclear spin, and $Q$ the quadrupole moment of the nucleus. By considering the hexagonal symmetry of the AlB$_2$ structure, we can assume that the in-plane anisotropy parameter $\eta = (V_{xx} - V_{yy})/V_{zz} = 0$ and, therefore, $V_{xx} = V_{yy}$. Since the $V_{i,j}$ tensor is traceless, by evaluating $eq = V_{zz}$ from the simulated $\nu_Q$ data [see Eq. (1)], we get $V_{zz} = 1.1 \times 10^{20} \text{ Vm}^{-2}$ and $V_{xx} = V_{yy} = -5.5 \times 10^{19} \text{ Vm}^{-2}$.
TABLE I. Key NMR parameters for the investigated samples compared with those of AlB₂ and MgB₂ [24].

| Material      | Shift (ppm) | $T_1 T$ ($10^4$ s K) | $S_0$ ($10^{-4}$ s K) |
|---------------|-------------|----------------------|-----------------------|
| ZrB₂          | 120         | 1.81 ± 0.07          | 2.60 ± 0.18           |
| Zr₀.₉₆V₀.₀₄B₂ | 120         | 1.89 ± 0.07          | 2.72 ± 0.11           |
| HfB₂          | 140         | 1.67 ± 0.05          | 3.27 ± 0.12           |
| Hf₀.₉₆V₀.₀₄B₂ | 140         | 1.56 ± 0.07          | 3.06 ± 0.09           |
| AlB₂          | -10         | 0.14 ± 0.04          | 0.009 ± 0.001         |
| MgB₂          | 70          | 0.018 ± 0.006        | 0.009 ± 0.001         |

As summarized in Table I, the Knight shift values are of the same order of magnitude as in MgB₂ [19,24,26,27], but we note a difference of two orders of magnitude in the density of states (DOS) at the Fermi level compared with those of AlB₂ and MgB₂ [24].

The raw data, i.e., $^{11}$B NMR $T_1^{-1}$ inverse saturation recovery curves, for the temperatures above $T_c$ were fitted by assuming the standard magnetization recovery formula for a single spin-lattice relaxation time [25]. However, due to the expected high anisotropy of $\mu_0H_{ab}$, and by analogy with MgB₂ [5], in powder samples we expect grains with different orientations, i.e., where the applied magnetic field lies in the $ab$ plane or is parallel to the $c$ axis. $A priori$ the orthogonal and parallel magnetic susceptibilities and the upper critical field depend on the direction of the field. The existence of nonequivalent grains, due to the anisotropy of the upper critical field, is also confirmed by magnetometry (Fig. 4) and resistivity (Fig. 8) measurements, which show a superconducting width transition $\Delta T$ $\sim$ 2.5 K, hence suggesting the persistence of inhomogeneous domains. In a first approximation and following a procedure employed in the MgB₂ case [24,27], we can fit the data, by assuming two relaxation processes [see Eq. (2)], related to the normal phase and to the superconducting phase, respectively:

$$I(t_d) \propto \alpha \exp(t_d/T_{1s})^\beta + (1 - \alpha) \exp(t_d/T_{1n})^\beta.$$  (2)

Here $t_d$ is the time delay in the NMR pulse sequence, $T_{1s}$ and $T_{1n}$ the spin-lattice relaxation times of the superconducting and normal grains, respectively, $\alpha$ the superconducting volume fraction and $\beta$ the stretching parameter (close to 1 in this case). We assume that $\alpha$ is a temperature-dependent fit parameter, ranging from $\sim 1$ (in case of maximum superconducting fraction, as evaluated from magnetometry data), down to 0.

In the transition region the two plateaux are connected with a sigmoidal function.

The $T_1^{-1}(T)$ spin-lattice relaxation data above $T_c$ follow the linear behavior in $T$ of a simple metal (see Fig. 5), where nuclear relaxation occurs mostly via interactions with the conduction electrons. On the other hand, below $T_c$, the superconducting grains may exhibit two trends: a power-law with an integer exponent, typical of anisotropic superconductors, or an exponential trend, as expected for s-wave superconductors. If the sample is not perfectly homogeneous, a second relaxation component could persist as a linear trend associated to normal grains, as shown in Fig. 6. The hypothesis of the two relaxation times is justified by the good fit results that we obtain for the evaluation of spin-lattice relaxation rates $R_1 = T_1^{-1}$. A quantitative analysis is, however, hampered by a contribution to the relaxation from the flux vortex lines (i.e., their thermal motion) [28,29]. Since we performed a field cooling (FC) measurement, the formation of a flux line lattice (FLL) with a regular arrangement of vortices, mostly with hexagonal symmetry, is expected. The geometric parameter of this lattice is the intervortex spacing $d(\mu_0H) = (2\Phi_0/3\mu_0H)^{1/2}$, which implies $d(3.505T) = 26$ nm in our case. This value is approximately six times the diameter of the vortices $\xi$, as evaluated in Sec. IV C, implying that the measured $T_1$ values consist of the sum of a slow contribution from outside the vortex cores and a faster contribution from the normal region within the vortices [29].

We speculate that the considerable anisotropy of the upper critical field of MgB₂ [5] is also a characteristic of our materials. A rigorous confirmation would be obtained by relevant experiments on single crystals via, e.g., thermal conductivity measurements. In general, s-wave superconductors exhibit an exponential decrease of $T_1^{-1}(T)$ well below $T_c$, from which the gap value $\Delta$ can be extracted. The appearance of a Hebel-Slichter coherence peak is usually interpreted as
confirming the Cooper-pairing with spherical symmetry. In our case, the absence of a coherence peak does not rule out an $s$-wave parity since the size of the peak can be significantly reduced by the pair-breaking mechanism in the presence of high fields [30]. Due to the above-mentioned complexity of the relaxation processes and the quality of our data, it is impossible to extract the gap value $\Delta$ from the exponential decrease of the spin-lattice relaxation time. In any case, a first evidence for $s$-wave superconductivity is the increasing deviation from a power-law behavior with an exponent 3 towards lower temperatures (see Fig. 6). To justify the similarities between the phonon-mediated $s$-wave superconductivity mechanism in MgB$_2$ and our V-doped samples we note that vanadium, given its 3$d^3$ orbital, has one more electron, if compared to Zr (4$d^2$) and Hf (5$d^2$). An analogous electron doping is confirmed in the case of MgB$_2$, where the $s$ states of Mg are pushed up by the boron $p_z$ orbitals and, therefore, fully donate their electrons to the boron-derived conduction band [4]. This doping mechanism occurs also in the opposite direction (reduction of the $T_c$ value) in MgB$_2$. In this case, both the substitution of Mg with Li (hole doping) and of boron with carbon or Al (electron doping) reduce the $T_c$ of the material [31]. In this case, it is claimed that the electrons fill the $\sigma$ band and holes occupy the $\pi$ band, therefore making charge compensation impossible. Furthermore, a recent paper [32] supported the hypothesis of two gaps in Zr$_{0.96}$V$_{0.04}$B$_2$ from critical current density $J_c$ measurements in different fields. In fact, $J_c$ can suitably be fitted by the sum of two contributions $J_1$ and $J_2$, respectively, related to the first and the second gap, following an exponential trend as a function of the applied magnetic field.

FIG. 6. $^{11}$B NMR $1/T_1(T)$ data at 3.505 T for Zr$_{0.96}$V$_{0.04}$B$_2$ (main plot) and Hf$_{0.97}$V$_{0.03}$B$_2$ (inset), representing the two relaxation times of Eq. (2), which result from fitting the inversion recovery curves. Both superconducting samples exhibit a conventional metallic trend (red points) and a superconducting dropdown (magenta points). The blue lines are power laws with critical exponent 3, that would be a signature of $d$-wave superconductivity. In both samples we argue that the faster relaxation rates below 5.5 K with respect to the power-law support the hypothesis of $s$-wave pairing.

Superconducting quantum interference device (SQUID) magnetometry measurements were made on all the samples (ZrB$_2$, HfB$_2$, Zr$_{0.96}$V$_{0.04}$B$_2$, and Hf$_{0.97}$V$_{0.03}$B$_2$). The high sensitivity ($10^{-9}$ A m$^{-2}$) of the reciprocating sample option (RSO) of the MPMS magnetometer allowed us to detect small impurities. In particular, in the ZrB$_2$ and Zr$_{0.96}$V$_{0.04}$B$_2$ samples a small mass fraction of about 0.5% exhibits a superconducting transition at 5.5 K, the typical $T_c$ of ZrB$_{12}$ impurities. Smaller impurity contributions are also visible from the $\chi(T)$ plots at fields between 0.1 and 7 T, exhibiting a steady increase below 20 K. Therefore, an accurate measurements of $T_c(H = 0)$ was achieved by applying a small magnetic field of 1 mT. The obtained values of $T_c$ are 8.33 K for Zr$_{0.96}$V$_{0.04}$B$_2$ and 7.31 K for Hf$_{0.97}$V$_{0.03}$B$_2$. As shown in the inset of Fig. 7, the typical type-II SC cycles can be observed below $T_c$; above $T_c$, a clear diamagnetic trend is confirmed with a typical $\chi_m = -7.5 \times 10^{-10}$ m$^3$mol$^{-1}$, a value approximately five times smaller than bismuth.

The low-field region (from 0.2 to 6 mT), exhibits an initial linear trend in $M(H)$. It is possible to extract an approximate value of $\mu_0 H_{c1}$, defining it as the field at which the deviation from the linear trend (called Meissner line) exceeds the sensitivity of the instrument. Performing this analysis, for each of the $M$ versus $H$ curves, we obtain $\mu_0 H_{c1}(T)$, as shown in Fig. 7 for both Zr$_{0.96}$V$_{0.04}$B$_2$ and Hf$_{0.97}$V$_{0.03}$B$_2$. According to the two-band Ginzburg-Landau theory applied to MgB$_2$, the lower critical field exhibits a change in concavity (from negative to positive, upon cooling) at $T_c = 0.5$ [33]. Since this change is scarcely distinct and the model depends upon the interband mixing of the two order parameters and of their gradients, it is difficult to interpret the $\mu_0 H_{c1}(T)$ trend which, as reported in the literature for MgB$_2$ [34,35] can be fitted even with a line. On the other hand, the previously reported Zr$_{0.96}$V$_{0.04}$B$_2$ data [7] show a pronounced upturn, which is not
Zr_0 present in our case. The reason for this discrepancy is unclear at the moment.

C. Resistivity

Systematic resistivity measurements were performed in zero field on all the samples (ZrB_2, HfB_2, Zr_{0.96}V_{0.04}B_2, and Hf_{0.97}V_{0.03}B_2), as shown in Fig. 8, and on the superconducting samples Zr_{0.96}V_{0.04}B_2 (see the inset of Fig. 8) and Hf_{0.97}V_{0.03}B_2 in magnetic fields up to 7 T.

Each resistance measurement in zero field (ZF) was performed from 2 to 310 K, while in field we focused our attention on the superconducting transition region (range from 2 to 10 K). Due to the small resistivity values, i.e., \( \rho(T_c) \approx 0.7 \mu \Omega \text{cm} \) for Zr_{0.96}V_{0.04}B_2 and 0.8 \( \mu \Omega \text{cm} \) for Hf_{0.97}V_{0.03}B_2, we argue that we can analyze our data within the clean limit approximation.

Based on the data at different fields, the \( \mu_0 H_{c2}(T) \) values were evaluated (see Fig. 9). According to the theory of Werthamer, Helfand, and Hohenberg (WHH) [36], in the clean limit [37] and for small spin-orbit couplings [38] we have

\[
\mu_0 H_{c2}(0) = -0.73 T_c \frac{d H_{c2}}{dT} \bigg|_{T=T_c}. \tag{3}
\]

Within this approximation, \( \mu_0 H_{c2}(T) \) can be fitted with a parabolic curve

\[
\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0) [1 - (T/T_c)^2]. \tag{4}
\]

From the Ginzburg-Landau formula \( \xi(0) = [\phi_0/(2\pi \mu_0 H_{c2}(0))]^{1/2} \), our estimate of the coherence lengths \( \xi(0) \) in both Zr_{0.96}V_{0.04}B_2 and Hf_{0.97}V_{0.03}B_2 are present.

we finally obtain the Ginzburg-Landau \( \kappa \) parameter, with a value of 125 for Zr_{0.96}V_{0.04}B_2 and 80 for Hf_{0.97}V_{0.03}B_2, respectively, indicating the strong type-II nature of these superconductors. From \( \kappa = \lambda/\xi \), the London penetration depth \( \lambda(0) \) in the two materials, is 570 and 445 nm, respectively.

D. Muon-spin rotation results in the SC phase

Values of similar magnitude for the magnetic field penetration depth were obtained from preliminary muon-spin rotation (\( \mu \)SR) experiments on Zr_{0.96}V_{0.04}B_2 (see Fig. 10). Once implanted in matter, spin-polarized muons act as microscopic probes of magnetism, which upon decay emit positrons preferentially along the muon-spin direction. From the spatial anisotropy of the emitted positrons (i.e., the asymmetry signal) one can reveal the distribution of the local magnetic fields [39,40]. In our case, by applying 0.6 T, a regular flux-line lattice (FLL) develops in the superconducting phase below \( T_c \). By uniformly sampling the FLL, muons experience an additional relaxation \( \sigma_{sc} \), which is related to the absolute magnetic penetration depth \( \lambda \) via [41,42]

\[
\frac{\sigma_{sc}^2}{\gamma_\mu} = 0.00371 \cdot \frac{\Phi_0^2}{\lambda^4}. \tag{5}
\]

Here \( \Phi_0 = 2.068 \times 10^{-3} \text{T m}^2 \) is the magnetic flux quantum and \( \gamma_\mu = 2\pi \times 135.53 \text{ MHz/T} \), the muon gyromagnetic ratio.
considerably distorted vortex lattice leading to a strong decay of the muon asymmetry and hence underestimated $\lambda_{ab}(0)$ values. However, since in fields exceeding 0.3 T, only weak or no pinning effects were observed, we are confident that by applying a transverse field of 0.6 T, our results reflect the penetration depth.

V. SUMMARY AND CONCLUSION

From SQUID magnetometry, NMR, resistivity, and preliminary $\mu$SR experiment data on ZrB$_2$, HfB$_2$, Zr$_{0.96}$V$_{0.04}$B$_2$, and Hf$_{0.97}$V$_{0.03}$B$_2$, we argue that the latter two samples are $s$-wave superconductors, resulting from electron doping via d orbitals of vanadium. On the other hand, in MgB$_2$ the peculiar self-doping exists thanks to the boron-related electrons at the Fermi level; at the same time also the s states of Mg donate their electrons to the boron-derived conduction bands (metallic B). It is also worth mentioning that B vacancies (a common defect occurring in diborides) enhance the DOS (a common defect occurring in diborides) enhance the DOS

Figure 10 shows the temperature dependence of $\sigma_{xy}$, proportional to the superfluid density [$\sigma_{xy} \propto n_s \propto \lambda^{-2}(T)$], together with a numerical fit with an average-field model $1/\lambda^2(T) = [1/\lambda^2(0)][1 - (T/T_c)^2]$, which gives $1/\lambda^2(0) = 1.43 \pm 0.2 \, \mu\text{m}^{-2}$ and $n = 2.0 \pm 0.1$. Subsequently, by using the relation $\lambda_{ab}(0) = \lambda_{\text{eff}}(0)/1.31$, we estimate the in-plane magnetic penetration depth $\lambda_{ab}(0) = 638 \pm 11$ nm. This value is close to the one determined via macroscopic methods (see above), but it is very different from $\lambda_{ab}(0) = 100$ nm, also measured via $\mu$SR in MgB$_2$ [18]. This difference can be accounted for by considering the rather small electronic density of states in Zr$_{0.96}$V$_{0.04}$B$_2$ compared to that in MgB$_2$, compatible with the very different NMR relaxation-rate values reported in Table I.

As a final note, we recall that the choice of the applied transverse field is crucial for the correct determination of the field penetration depth. Indeed, detailed studies of the magnetic field dependence of the muon-spin depolarization rate in MgB$_2$ (see, e.g., Figs. 1 and 2 in Ref. [18]) have shown strong pinning effects in low applied fields (below 0.3 T). These imply a

FIG. 10. Transverse-field $\mu$SR data in the superconducting phase of Zr$_{0.96}$V$_{0.04}$B$_2$ in a magnetic field $\mu_0 H = 0.6$ T.

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