Surface contribution to the superconducting properties of MgB$_2$ single crystals

A. Rydh, U. Welp, J. M. Hiller, A. Koshelev, W. K. Kwok, and G. W. Crabtree
Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

K. H. P. Kim, C. U. Jung, H.-S. Lee, B. Kang, and S.-I. Lee
NCRICS and Dept. of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

(Dated: March 22, 2022)

We demonstrate direct evidence of possible surface superconductivity on small, well-shaped MgB$_2$ single crystals. Transport measurements in the range $H < 1.6H_{c2}$, where $H_{c2}$ is the bulk upper critical field for the $c$ axis, show non-Ohmic and strongly angular dependent resistivity. Studies of the alignment of $H$ with selected crystal surfaces, transport and specific heat measurements on the same crystal, and a physical sculpturing of the crystal surfaces using a focused ion beam all support the conclusion. Similar, albeit less pronounced results are obtained for fields in the basal plane.

PACS numbers: 74.25.Dw, 74.25.Fy, 74.25.Op, 74.25.Qt

Keywords: surface superconductivity, transport, specific heat, phase diagram, FIB, peak effect

The binary MgB$_2$ compound has been subject of intense studies since the discovery of its superconducting properties at temperatures up to 39 K. The superconductor has been found to be of phonon-mediated BCS type but with a multitude of novel properties, mainly arising from its complex, two-band ($\pi$ and $\sigma$) Fermi surface. In particular, MgB$_2$ is the first example of a superconductor showing two distinct superconducting gaps. The two-gap nature is revealed in the macroscopic properties of MgB$_2$ through a pronounced temperature dependence of the anisotropy of the upper critical field. The effect of the two-gap structure on vortex dynamics is presently under intense investigation. Although STM and specific heat measurements indicate a rapid suppression of the $\pi$ gap with increasing magnetic field its effect on magneto-transport properties remains controversial. In particular, a pronounced broadening of the resistive transitions in magnetic fields applied along the $c$ axis has been observed. Whether this broadening is related to the two superconducting gaps or other phenomena such as vortex dissipation and vortex lattice melting, surface barriers, superconducting fluctuations, or surface superconductivity remains to be settled.

In this Letter we present definitive indications of a surface superconducting state in well-shaped MgB$_2$ single crystals. From angular dependent transport and specific heat measurements, we demonstrate that the broadening of the resistive transitions for $H \parallel c$ as well as for $H \parallel ab$ occurs above the bulk upper critical field, while there is virtually no broadening of the transitions in the mixed state. The result is confirmed by directly modifying the crystal surface geometry using a focused ion beam (FIB).

MgB$_2$ crystals with typical maximum dimensions of 50 $\mu$m were obtained through a high pressure heat treatment of a mixture of Mg and B in excess Mg. The resulting crystals were well shaped with smooth, hexagonal facets. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy confirmed the absence of grain boundaries or other correlated defects. The crystals had $T_c \approx 36$ K, $\Delta T_c \approx 0.15$ K (at low current), and a bulk $H_{c2}(0) \approx 3.5$ T. Transport measurements were performed using standard DC and AC techniques. A total of five crystals were studied, all showing similar behavior with slight variations in the exact shape of the resistive transition. We present results on two of these crystals.

Figures a and b show the resistive transitions in various fields around the $c$ axis and around the basal ($ab$) plane, respectively. The transitions broaden significantly with increasing field around $c$ as reported earlier. This broadening evolves in a characteristic two stage fashion with a gradual onset at $T_{on}$ and a steep drop at lower temperature, which we are going to identify with $T_{c2}(H)$. The gradual onset broadens in increasing field, while the steep drop at $T_{c2}(H)$ stays sharp. In addition to a strong current dependence the broadening is also strongly angular dependent. As the applied field is tilted away from the $c$ axis the gradual resistive onset is rapidly suppressed and the steep resistive drop becomes more pronounced. The gradual onset is largely eliminated at angles around 40$^\circ$ (in 1.5 T). Similar behavior is seen for fields applied along the $ab$ plane (Fig. c).

For exact field alignment with the $ab$ plane, the gradual resistive onset becomes more pronounced with increasing fields, but is readily suppressed by a tilt as small as 0.7$^\circ$. The strong angular dependence is clearly seen in angular scans shown in Fig. d for both the $c$ axis (main panel) and the $ab$ plane (inset). The angular dependence around the $c$ axis depends on the direction in which the field is tilted. If the field is tilted across the vertical side faces (the direction marked as “$\perp$” in the schematic inset of Fig. d) the resistance increases rapidly in a cusp-like fashion. At high angles the resistance decreases again due to the super-imposed, intrinsic, superconducting anisotropy. If
the field is tilted in such a way that it stays parallel to the side surfaces (marked as "∥" in Fig. 1h) the resistance remains at a low level. As a direct proof that the resistive behavior shown in Fig. 1 is associated with the sample surfaces, we artificially modified the side faces of a crystal. A trapezoidal cross-section was cut into the sample surfaces, we artificially modified the side faces.

It is important to note that the angular dependent, gradual, superconducting onset at $T_{on}$ in Figs. 1 and 2 occurs well above the bulk upper critical field. Figure 3 shows the specific heat signature of $T_{c2}$ together with the resistive transition of the same crystal measured at various currents in a field of 1.5 T $∥$ c. The step in $\Delta C_p/T$, which corresponds to the bulk superconducting transition, occurs about 5 K below $T_{on}$ (for $H = 1.5$ T) but coincides well with the steep drop to zero resistance seen at high enough currents. This indicates that the transport behavior is caused neither by a conventional surface barrier effect [13], nor by a transition in the vortex system [16] for which the sample has to be in the mixed state, i.e., below $H_{c2}$. Instead, the normal conducting bulk is covered by a superconducting sheath in places where the field is aligned with the surface.

The field – temperature ($H$–$T$) phase diagram resulting from the data of Figs. 1 and 2 and similar data is shown in Fig. 4 and is in agreement with previous reports [14, 15, 16]. Shown are the bulk upper critical fields, as determined from specific heat measurements and resistive drops, as well as the onsets of angular and current depend transport. We notice that the onsets are enhanced with respect to the bulk $H_{c2}$ by a coefficient of about 1.6 for $H \parallel c$ and 1.4 for $H \parallel ab$. This behavior is reminiscent of the development of a surface superconducting state. A superconducting surface sheath with a thickness given by the Ginzburg–Landau coherence length, $\xi(T)$, nucleates at an enhanced field of $H_{c3} = 1.69H_{c2}$ when a magnetic field is applied parallel to the flat (infinite) surface of an isotropic superconductor [17]. The exact value of the enhancement factor may depend on clean-limit corrections [17], on the shape of the sample and its intrinsic
anisotropy [18], and on the surface quality [20].

The results presented here can be accounted for in a model of surface superconductivity. It has been shown that the surface superconducting state is rapidly suppressed in a cusp-like fashion when the applied field has a normal component to the surface [19], exactly the behavior observed when the field is tilted across the side face (see Figs. 1 and 2). Similarly, when the field is tilted within the side faces the surface superconducting state is not suppressed, and the only observed angular dependence arises from the intrinsic anisotropy of MgB$_2$. Furthermore, non-Ohmic transport properties above the bulk upper critical field are expected due to the presence of a surface critical current, $I_{sc}$ [20]. If the applied current is smaller than $I_{sc}$ then the resistance will go to zero above $H_{c2}$ ($T_{c2}$), see Fig. 3. At higher current a finite, current dependent resistance arises signaling current sharing between the surface sheath and the normal core of the sample. At $H_{c2}$ the core of the sample goes superconducting, and the resistance drops to zero. We also note that (for macroscopic samples) the contribution of the superconducting surface sheath has a negligible contribution to the specific heat.

Figure 4 and 5 suggest the surprising result that the surface superconducting state is more pronounced and (as function of angle) more robust for $\mathbf{H} \parallel \mathbf{c}$ than for $\mathbf{H} \parallel \mathbf{ab}$, implying that surface supercurrents on the narrow side faces (shaded in Fig. 1b) are stronger than those on the wide top and bottom faces. A similar observation has recently been reported for NbSe$_2$ [22] for which indications of surface superconductivity were obtained for $\mathbf{H} \parallel \mathbf{c}$ but not for $\mathbf{H} \parallel \mathbf{ab}$. Several factors may contribute to this behavior. The top and bottom surfaces appear very smooth indicating that the surface critical currents are weak. This is consistent with the broader angular dependence for field around the $c$ axis and studies on PbTl films and ribbons [20] that have shown that the angular dependence is sharper for smooth surfaces. In addition, due to the anisotropy of the coherence length, the thickness of the current carrying layer at the top and bottom faces is about four times smaller than along the side faces.

To complete the picture, we studied the influence of the angle between the magnetic field and the current direction on the transport properties, for $\mathbf{H}$ aligned with the basal plane. Figure 5 shows the field dependence of the resistance for $\mathbf{H} \perp \mathbf{I}$ and $\mathbf{H} \parallel \mathbf{I}$. A distinct orientational dependence is observed, reminiscent of the Lorentz force effect on a vortex system. In the parallel case the transitions are featureless, while for $\mathbf{H} \perp \mathbf{I}$ the location of $H_{c2}$ is revealed by the already described, steep drop of the resistance and the appearance of a peak effect at high enough currents. The angular dependence clearly persists to fields well above $H_{c2}$. In considering the surface superconductivity description, the angular-dependence behavior arises because the mutual orientation of $\mathbf{H}$ and $\mathbf{I}$ affects the distribution of the superconducting order parameter near the surface [23]. For $\mathbf{H} \perp \mathbf{I}$ the superconducting order parameter is displaced with respect to the surface [24] whereas for $\mathbf{H} \parallel \mathbf{I}$ it acquires an additional phase analogous to the force free configuration in thin, superconducting wires. As a result there is an intrinsic anisotropy of the superconducting phase stiffness and, consequently, of the maximum (depairing) critical current $I_{c}^{\perp}/I_{c}^{\parallel} = 0.6$ which can account for our data.

Surface superconductivity as discussed here is a con-
sequence of the boundary conditions at the free surface of an otherwise unperturbed sample. In the case of MgB$_2$, ARPES experiments [22] show that the very existence of the surface induces modifications of the electronic structure at Mg- and B-terminated surfaces. Various band structure calculations [26] indicate that these surface electronic states could either locally enhance or suppress the superconducting properties. However, increasing the surface area by pulverizing single crystals has not given any indication for enhanced $T_c$ [27]. In addition, the sample surfaces could be modified due to exposure to oxygen and humidity. Although the value of $T_c$ has proven remarkably insensitive to modest amounts of disorder [28], there could arise a shell of enhanced (dirty) upper critical field giving rise to the observed transport behavior. However, our experiments on the freshly cut surfaces seem to rule out such a possibility. Furthermore, the observation of the general features shown here with enhancement factors consistently in the range of 1.5 to 2 on a large number of crystals from various sources indicates an intrinsic nature of the surface effects.

In summary, we have shown that the surfaces of well-shaped MgB$_2$ single crystals possess locally enhanced superconducting properties in magnetic fields aligned to the surfaces. The surface superconductivity is more pronounced for fields along the $c$ axis and is found to display a field-induced anisotropy for fields in the basal plane. Further studies could address the possible significance of the two-band structure for the exact mechanism behind the observations.

This work was supported through the Fulbright program and the Sweden-America Foundation (A.R.), by the Ministry of Science and Technology of Korea, and by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Work with the FIB was carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439.

* Also at Solid State Physics, Royal Institute of Technology (KTH), Stockholm-Kista, Sweden; Electronic address: rydh@anl.gov

[1] J. Nagamatsu et al., Nature (London) 410, 63 (2001). For extensive reviews see Special Edition on MgB$_2$, Physica (Amsterdam) 385C (2003).
[2] H. J. Choi et al., Nature (London) 418, 758 (2002).
[3] A. Y. Liu et al., Phys. Rev. Lett. 87, 087005 (2001).
[4] F. Bouquet et al., Phys. Rev. Lett. 87, 047001 (2001); P. Szabo et al., ibid 87, 137005 (2001); F. Giubileo et al., ibid 87 177008 (2001); H. Schmidt et al., ibid 88, 127002 (2002); M. Iavarone et al., ibid 89, 187002 (2002).
[5] M. Angst et al., Phys. Rev. Lett. 88, 167004 (2002); S. L. Budko et al., Phys. Rev. B 64, 180506 (2001); M. Zehetmayer et al., ibid 66, 052505 (2002); Y. Machida et al., ibid 67, 094507 (2003).
[6] L. Lyard et al., Phys. Rev. B 66, 180502 (2002).
[7] U. Welp et al., Phys. Rev. B 67, 012505 (2003).
[8] A. V. Sologubenko et al., Phys. Rev. B 65, 180505 (2002).
[9] M. Eskildsen et al., Phys. Rev. Lett. 89, 187003 (2002).
[10] F. Bouquet et al., Phys. Rev. Lett. 89, 257001 (2002)
[11] A. K. Pradhan et al., Phys. Rev. B 65, 144513 (2002); Yu. Eltsev, Physica (Amsterdam) 385C, 162 (2003).
[12] Yu. Eltsev et al., Physica (Amsterdam) 378–381C, 61 (2002); Yu. Eltsev et al., Phys. Rev. B 65, 140501 (2002).
[13] T. Masui et al., cond-mat/0210358.
[14] C. U. Jung et al., Phys. Rev. B 66, 184519 (2002).
[15] K. H. Kim et al., Phys. Rev. B 65, 100510 (2002).
[16] D. Saint-James and P. G. de Gennes, Phys. Lett. 7, 306 (1963); A. A. Abrikosov, Sov. Phys. JETP 20, 480 (1965); H. J. Fink, Phys. Rev. Lett. 14, 309 (1965).
[17] C.-R. Hu and V. Korenman, Phys. Rev. 178, 684 (1969); Phys. Rev. B 6, 1 (1972).
[18] V. G. Kogan et al., Phys. Rev. B 65, 094514 (2002).
[19] C. Hempstead and Y. Kim, Phys. Rev. Lett. 12, 145 (1964); W. J. Tomash and A. S. Joseph, Phys. Rev. Lett. 12, 148 (1964); R. S. Thompson, Sov. Phys. JETP 42, 1144 (1976).
[20] H. R. Hart, Jr., and P. S. Swartz, Phys. Rev. 156, 403 (1967).
[21] I. O. Kulik, Soviet Phys. JETP 28, 461 (1969).
[22] G. D’Anna et al., Phys. Rev. B 54, 6583 (1996).
[23] H. Schmidt and H. J. Mikeska, J. Low Temp. Phys. 3, 123 (1970); A. E. Koshelev, to be published.
[24] This effect predicts rectification as seen, for example, in P. S. Swartz and H. R. Hart, Jr., Phys. Rev 156, 412 (1967). We could not observe any such effects here, however, possibly due to the contact arrangement.
[25] H. Uchiyama et al., Phys. Rev. Lett. 88, 157002 (2002); S. Souma et al., Nature 423, 65 (2003).
[26] I. G. Kim et al., Phys. Rev. B 64, 020508 (2001); V. M. Silkin et al., ibid 172512; E. Bascones and F. Guinea, ibid 214508; Z. Li et al., Phys. Rev. B 65, 100507 (2002); V. D. Serviedio et al., Phys. Rev. B 66, 140502 (2002); G. Profeta et al., ibid 184517.
[27] J. Karpinski, private communication.
[28] I. I. Mazin et al., Phys. Rev. Lett. 89, 107002 (2002).