s-wave superconductivity probed by measuring magnetic penetration depth and lower critical field of MgCNi3 single crystals

P. Diener1, P. Rodière1, T. Klein1,2, C. Marcenat3,4, J. Kacmarcik4, Z. Pribulova1, D.J. Jang5, H.S. Lee5, H.G. Lee6, S.I. Lee6

1 Institut Néel, CNRS/UJF 25 rue des Martyrs BP 166 38042 Grenoble cedex 9, FRANCE
2 Institut Universitaire de France and Université Joseph Fourier, B.P.53, 38041 Grenoble Cedex 9, France
3 CEA, Institut Nanosciences et Cryogénie, SPMS-LATEQS - 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
4 Safarik University, Slovak Academy Sciences, Institut of Experimental Physics, Center for Low Temperature Physics, Kosice 04001, Slovak
5 Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
6 National Creative Research Initiative Center for Superconductivity, Department of Physics, Sogang University, Seoul, Korea

The magnetic penetration depth \( \lambda \) has been measured in MgCNi3 single crystals using both a high precision Tunnel Diode Oscillator technique (TDO) and Hall probe magnetization (HPM). In striking contrast to previous measurements in powders, \( \delta \lambda(T) \) deduced from TDO measurements increases exponentially at low temperature, clearly showing that the superconducting gap is fully open over the whole Fermi surface. An absolute value at zero temperature \( \lambda(0) \sim 230 \text{ nm} \) is found from the lower critical field measured by HPM. We also discuss the observed difference of the superfluid density deduced from both techniques. A possible explanation could be due to a systematic decrease of the critical temperature at the sample surface.

PACS numbers: 74.25.Nf, 74.25.Op, 74.70.Dd

The interplay between magnetism and superconductivity is currently a subject of great interest. In the UGe2 and URhGe uranium compounds, for instance, a long range ferromagnetic ordered phase coexists with the superconducting phase and a mechanism of spin fluctuations (SF) could be at the origin of the Cooper pair formation \([1,2]\). The recent discovery of high temperature superconductivity in oxypnictides also rapidly became the topic of a tremendous number of both experimental and theoretical works. The parent undoped LnO-FeAs (where Ln=La,Sm,...) compound is here close to itinerant magnetism due to the presence of a high density of Fe d states at the Fermi level \([3]\), leading to competing ferromagnetic and antiferromagnetic fluctuations. Similarly in the cubic (anti-)perovskite MgCNi3 compound \([4]\), the presence of a strong Van Hove singularity in the density of Ni states slightly below the Fermi level also leads to strong ferromagnetic fluctuations \([5,6]\). These two systems have also a Fermi surface composed of both electron and hole pockets (3D sheets in MgCNi3 as compared to quasi-cylindrical sheets in oxypnictides).

Despite these striking similarities in their electronic and magnetic properties, spin fluctuations lead to very different effects in those systems. On the one hand, ab-initio calculations rapidly showed that the electron-phonon coupling constant \( \lambda_{e-ph} \sim 0.2 \) is far too low to account for the high critical temperatures observed in oxypnictides (up to \( \sim 55 \text{ K} \)) and an unconventional mechanism mediated by the SF associated with a sign reversal of the \( (s\)-wave) order parameter between electrons and holes sheets of the Fermi surface has been proposed \([10]\). On the other hand, it has been suggested that the narrow Van Hove singularity could be responsible for a nearly unstable phonon mode in MgCNi3 inducing a large, although reduced by SF, \( \lambda_{e-ph} \sim 1.1, 1.2 \) in agreement with experiments which yield an average electron-phonon coupling constant in the order of 1.7 \([11,13,14]\). The interplay between electron-phonon coupling and SF is further emphasized in this system by the existence of a large isotopic effect \([12]\) which has been suggested to be enhanced by the strong SF \([12]\).

In this context, the nature of the superconducting order parameter rapidly became a crucial issue. In MgCNi3, the experimental results still remain controversial: on the one hand, penetration depth measurements (in polycrystalline samples) showed a quadratic, i.e. non \( s \)-wave, temperature dependence suggesting a nodal order parameter \([17]\), whereas specific heat measurements clearly indicate that the superconducting gap \( (\Delta) \) is fully open, with a \( \Delta/k_B T \) ratio ranging from 1.9 to 2.1 \([13,18,19]\) i.e. well above the BCS weak coupling 1.76 value.

In this paper, we present high precision magnetic penetration depth and lower critical field measurements performed in the same MgCNi3 single crystals. We show that \( \lambda(T) \) clearly follows an exponential temperature dependence for \( T < T_c/3 \) showing that the gap is fully open on the whole Fermi surface. A zero temperature \( \lambda_0 \) value of \( 230 \text{ nm} \), i.e. well above the London clean limit BCS value \( (\sim 60 \text{ nm}) \) has been deduced from first penetration field measurements, clearly suggesting the presence of strong mass renormalization and/or impurity scattering effects. Introducing this value into the TDO data however leads to a temperature dependence of the normalized superfluid density \( \rho_S(T)/\rho_S(0) = [1 + \delta \lambda(T)/\lambda_0]^2 \) which is different from the one directly deduced from the lower critical field \( (H_{c1} \propto ln(\kappa)/\lambda^2 \) where \( \kappa = \lambda/\xi \)). Possible reasons for this discrepancy are discussed.
Single crystals were grown in a high pressure furnace as described elsewhere [20]. AC specific heat have been performed on several samples of the same batch [21]. All the measured crystals show sharp superconducting transitions ($\Delta T_c \sim 0.2$ K) emphasizing the excellent bulk homogeneity of each crystal. We observed however a large dispersion of critical temperatures from sample to sample, between approximately 5.9 to 7.6 K, probably due to a slight Ni deficiency in the MgCNi$_3$ structure [20]. Three single crystals with a thickness of 0.1mm but different shapes and critical temperatures have been selected. Sample #A can be approximated by a disk with a diameter of 0.3mm. Samples #B and #C have a rectangular shape of 0.21$x$0.15 mm$^2$ and 0.24$x$0.36 mm$^2$ respectively. Samples #A and #B both present a bulk $T_c$ of 6.9 K and exhibit exactly the same behavior by TDO and HPM, whereas sample #C has the highest $T_c$ at 7.6 K.

The magnetic penetration depth has been measured with a high stability LC oscillator operating at 14 MHz, driven by a Tunnel Diode [22, 23]. The AC excitation field is below 1 µT and the DC earth magnetic field is screened by a demagnetized weak ferromagnet amorphous ribbon, ensured to work well below $H_{c1}$. The sample stage, placed at the bottom of a home-made He$^3$ refrigerator, is regulated between 0.5 K and 10 K, whereas the LC oscillator remains at fixed temperature. The superconducting sample is glued with vacuum grease at the stage, placed at the bottom of a sapphire cold finger, which can be extracted in-situ [24]. The small filling factor of the excitation coil by the superconducting sample ($\sim 0.01\%$) ensures a small perturbation of the circuit and the frequency shift $\delta f$ divided by the one induced by the extraction of the superconducting sample, $\Delta f_0$, is then proportional to the imaginary part of the surface impedance and hence to the magnetic penetration depth [23]. As shown in the inset of Fig. 1, all samples present a sharp superconducting transition at a critical temperature $T_c$ (defined by the onset of the frequency shift change) equal to 6.9 K (resp. 7.6 K) for sample #A (resp. sample #C) in good agreement with the $C_p$ measurements.

Fig. 1 displays the temperature dependence of the frequency shift, proportional to $\delta \lambda(T)$, compared to the results previously reported in powders [17]. The amplitude of the shift is 10 times larger in the case of the powder reflecting the fact that the surface on which the supercurrents are flowing is much larger in powders than in single crystals (for the same sample volume). It is important to note that the temperature dependence of $\lambda$ is strikingly different in single crystals than in powder for which a $T^2$ power law has been reported below 1.8 K. Such a dependence has been interpreted as an evidence for unconventional superconductivity [17] but our measurements do not support this scenario as a $T^2$ power law only very poorly describes the experimental data (see dashed line in Fig. 1).

A very good fit to our data is actually obtained assuming the low temperature approximation for clean type II superconductors with a fully open gap : $\lambda(T) \propto \sqrt{\Delta/k BT} e^{-\Delta/k_BT}$. This expression is valid for $k_BT < \Delta/5$, and leads to $\Delta/k_B = 11.6(1)$ K for sample #A (and B) and $\Delta/k_B = 12.3(1)$ K for sample #C. Note that this fitting procedure can lead to a slightly overestimated $\Delta$ value (up to 10%, depending on the range of the fit and the ratio between $\Delta$ and $T_c$) but unambiguously shows that the gap is fully open in good agreement with previous tunneling spectroscopy [22, 24], NMR [8], and specific heat measurements which led to $\Delta/k_B \approx 13.0(2)$ K, 10.5 K and 13 K, respectively.

However, fitting the low temperature data only leads to the size of the minimum superconducting gap. To unambiguously exclude the presence of any other gaps (and/or other gap symmetries) it is necessary to analyze the full temperature dependence of the normalized superfluid density $\rho_S(T) \propto 1/\lambda(T)^2$ up to $T_c$. This superfluid density can be deduced:

- either from the temperature dependence of the lower critical field : $H_{c1} = \Phi_0^2/(4\pi \lambda^2(Ln(\kappa) + c(\kappa)))$ where $\kappa = \lambda/\xi$ ($\xi$ being the coherence length) and $c(\kappa)$ a $\kappa$ dependent function tending towards 0.5 for large $\kappa$ values. As $\kappa$ is almost temperature independent (being in the order of 40), $H_{c1}(T)$ is directly proportional to the superfluid density which we will call $\rho_S^{TDO}$.

- or by introducing the absolute value of the penetration depth at $T=0$ K ($\lambda_0$) into the TDO data : $\rho_S^{TDO}(T) \propto \left[ \frac{1}{1 + 0.9 H(\lambda_0 / R)^2} \right]^{-2}$ = $\left[ \frac{1}{1 + 0.9 f(T)/H_0} \right]^{-2}$ where $R$ is a geometrical factor [28].

The local magnetic induction has been measured with
the penetration is much stronger close to the edges (probe 4), for several probe positions (see right inset) showing that, even 
∼ the same first penetration field (sample, respectively increased until a finite remanent field is obtained for different values of the applied field (measured on probe 2) through the sample corners). Probe 8 is located close to the center of the sample and probe 3, varying its orientation on the same single crystal of MgCNi₂P₂O₇, consistently with an isotropic cubic system.

For an isotropic superconducting gap, the BCS superfluid density

\[ \rho_S(T) \approx 1 - \frac{\partial f}{\partial E} \sqrt{E^2 - \Delta^2(T)} \]

where \( f \) is the Fermi Dirac distribution, \( E \) the energy above the Fermi energy, \( \Delta(T) \) the value of the superconducting gap at the temperature \( T \). As shown in Fig.3 (solid lines) very good fits to the gap equation \[32\] and taking \( \Delta(0) = 2k_B T_c \). Note that a superconducting gap equal to its weak coupling theory value \( \Delta(0) \approx 1.76k_B T_c \) only leads to a poor fit of the data, confirming the large value of the \( \Delta(0)/k_B T_c \) ratio previously obtained by bulk probes such as specific heat measurements.

On the other hand, \( \rho_S^{TDO} \) displays a strong downward curvature at low temperature followed by a clear upward curvature as the superfluid density drops below 0.5 (i.e. for \( \lambda(T) > 1.4\lambda_0 \)). As pointed out above one has to determine the \( \rho_S^{TDO}(T) \) in order to deduce \( \rho_S^{TDO}(T) \) from the \( \delta f / \Delta f \) data. The \( \rho_S^{TDO}(T) \) value has been calculated from the aspect ratio using the formula introduced by Prozorov \[28\]. The validity of this procedure has been checked on Pb samples. Moreover, different AC magnetic field orientations on the same single crystal of MgCNi₃₂O₇ show the same quantitative temperature dependence of \( \lambda(T) \), consistently with an isotropic cubic system.
A possible explanation would hence be an underestimation of $\lambda_0$. The influence of $\lambda_0$ is displayed in the inset of Fig.3. As shown taking $\lambda_0 \simeq 700 \text{ nm}$ instead of $230 \text{ nm}$ leads to a temperature dependence for $\rho_S^{\text{TDO}}$ similar to the one obtained for $\rho_S^{H_{c1}}$. This value is however well above our error bars on $\lambda_0$ and would correspond to $\mu_0 H_{c1}(0) \sim 15 \text{ G}$ i.e. even smaller than our first penetration field values ($\sim 55 \text{ G}$). Note that strong bulk pinning could lead to an overestimation of $H_p$, if measured in the center of the sample (see for instance [34]) but we checked that very similar $H_p$ values are obtained for several probe positions by placing the sample on an array of 11 miniature ($10 \times 10 \text{ pm}^2$) probes: as shown in the left inset of Fig.2, the field distribution clearly presents the $V - \text{shape}$ profile characteristic of a strong bulk pinning. Even though those profiles confirm the good homogeneity of the sample, one can not exclude the presence of a strong disorder at the surface of the samples leading to a surface penetration field much larger than the bulk value. However, the $\lambda_0=700 \text{ nm}$ value would require an extremely small mean free path ($\sim 1 \text{ nm}$, see discussion above). A possible difference between the mixed state and Meissner state penetration depth values associated either to a Doppler shift induced by the supercurrents on the excitation spectra [35, 36] or to a strong field dependence of $\lambda$ in the mixed state (see for instance [37]) due to multiband effects can be excluded in our isotropic, fully gapped system.

Another explanation could be a difference between bulk and surface critical temperature. Indeed, at low temperature TDO measurements only probe the sample on a typical depth in the order of $\lambda_0 \sim 0.2 \mu m$, i.e. roughly 0.4% of the total volume (for a Volume to Surface ratio of $50 \mu m$). In the presence of a weak coupling superconducting gap, this volume only increases to about 20% of the sample volume for $T \to T_c/2$ and the bulk of the sample is only probed close to $T_c$ as the magnetic penetration depth finally diverges for $T \to T_c$. On the other hand, the Hall probe has been placed close to the center of the sample in the HPM measurements and is hence sensitive to the bulk of the sample. In the case of MgCNi$_3$, it is known that the critical temperature has a surprising high sensitivity to a very small change in the C or Ni stoichiometry [1, 20] and also surface stress [14, 58]. Assuming that the critical temperature of the surface is 20% smaller than the bulk value, very good fit to the data could be obtained for $\rho_S^{\text{TDO}}$ using Eq.1 for $T < \frac{1}{2} T_c$ (still taking $\Delta(0) = 2k_B T_c$, see solid lines in Fig.3). Note that a large dispersion of the $T_c$ values in powder might explain the anomalous temperature dependence observed in previous A measurements. Clear deviations from the standard BCS theory (Eq.1) have been observed in systems like MgB$_2$ [39] or more recently in pnictides [40] but in our case those deviations in $\rho_S^{\text{TDO}}$ are due to surface inhomogeneities (disorder and/or $T_c$) and our measurements emphasize the importance of coupling complementary experimental probes in order to unambiguously address this issue.

To conclude, we have shown that the temperature dependence of the magnetic penetration depth is exponential in MgCNi$_3$ single crystals signalling the presence of a fully open superconducting gap. A drastically different behavior has systematically been observed between the superfluid density extracted from the lower critical field and TDO measurements performed on the same sample, which are most probably due to surface disorder and/or a depletion of 20% of the critical temperature at the surface.

We are most obliged to V. Mosser of ITRON, Montrouge, for the development of the Hall sensors used in this study. This work was partially supported by the Slovak R&D Agency under Contracts No. VVCE-0058-07, No. APVV-0346-07, and No. LPP-0101-06.

![Figure 3: (Color online) Normalized superfluid density deduced from $H_{c1}$ measurements (full symbols) and TDO measurements with $\lambda_0=230 \text{ nm}$ (open symbols) for samples #A (blue squares) and #C (red circles). The solid lines are the fit for a superconducting gap $\Delta = 2k_B T_c$ with $T_c \simeq 4.8, 5.6, 6.2$ and $7 \text{ K}$ (see text). Inset: influence of the $\lambda_0$ value used to deduce $\rho_S$ from TDO measurements.](image)

---

[1] D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J. P. Brison, E. Lhotel, and C. Paulsen, Nature 413, 613 (2001).

[2] S. Saxena, P. Agarwal, K. Ahilan, F. Grosche, R. Haselwimmer, M. Steiner, E. Pugh, I. Walker, S. Julian, P. Monthoux, et al., Nature 406, 587 (2000).
[3] D. Singh and M. H. Du, Phys. Rev. Lett. 100, 237003 (2008).
[4] T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, H. M. A., M. K. Haas, J. S. Slusky, K. Inumara, et al., Nature 411, 54 (2001).
[5] S. B. Dugdale and T. Jarlborg, Phys. Rev. B 64, 100508 (2001).
[6] H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett, and E. Tosatti, Phys. Rev. Lett. 88, 027001 (2001).
[7] D. Singh and I. Mazin, Phys. Rev. B 64, 140507 (2001).
[8] P. M. Singer, T. Imai, T. He, M. A. Hayward, and R. J. Cava, Phys. Rev. Lett. 87, 257601 (2001).
[9] L. Shan, Z. Y. Liu, Z. A. Ren, G. C. Che, and H. H. Wen, Phys. Rev. B 71, 144516 (2005).
[10] I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
[11] A. Y. Ignatov, S. Y. Savrasov, and T. A. Tyson, Phys. Rev. B 68, 220504 (2003).
[12] C. T. Van Degrift, Rev. Sci. Inst. 46, 599 (1975).
[13] A. Carrington, I. J. Bonalde, R. Prozorov, R. W. Gianetta, A. M. Kini, J. Schlueter, H. H. Wang, U. Geiser, and J. M. Williams, Phys. Rev. Lett. 83, 4172 (1999).
[14] R. Prozorov, R. Giannetta, A. Carrington, P. Fournier, R. Greene, P. Gutzsarma, D. Hinks, and A. Banks, Appl. Phys. Lett. 77, 4202 (2000).
[15] J. D. Fletcher, A. Carrington, P. Diener, P. Rodière, J. P. Brison, R. Prozorov, T. Olheiser, and R. W. Giannetta, Phys. Rev. Lett. 98, 057003 (2007).
[16] L. Shan, H. J. Tao, H. Gao, Z. Z. Li, Z. A. Ren, G. C. Che, and H. H. Wen, Phys. Rev. B 68, 144510 (2003).
[17] R. Prozorov, R. W. Giannetta, A. Carrington, and F. M. Araujo-Moreira, Phys. Rev. B 62, 115 (2000).
[18] E. H. Brandt, Phys. Rev. B 59, 3369 (1999).
[19] E. Zeldov, A. I. Larkin, V. B. Geshkenbein, M. Konczykowski, D. Majer, B. Khaykovich, V. M. Vinokur, and H. Shtrikman, Phys. Rev. Lett. 73, 1428 (1994).
[20] G. MacDougall, R. Cava, S. Kim, P. Russo, A. Savici, C. Wiebe, A. Winkels, Y. Uemura, and G. Luke, Physica B 374-375, 263 (2006).
[21] X. F. Lu, L. Shan, Z. Wang, H. Gao, Z. A. Ren, G. C. Che, and H. H. Wen, Phys. Rev. B 71, 174511 (2005).
[22] H. Padamsee, J. Neibor, C. Shiffman, JLTP 12, 387 (1973).
[23] R. Okazaki, M. Konczykowski, C. J. van der Beek, T. Kato, K. Hashimoto, M. Shimosawa, H. Shishido, M. Yamashita, M. Ishikado, H. Kito, et al., Phys. Rev. B 79, 064520 (2009).
[24] S. Yip and J. Sauls, Phys. Rev. Lett. 69, 2264 (1992).
[25] D. Xu, S. K. Yip, and J. A. Sauls, Phys. Rev. B 51, 16233 (1995).
[26] T. Klein, L. Lyard, J. Marcus, Z. Holanova, and C. Marcenat, Phys. Rev. B 73, 184513 (2006).
[27] M. Uehara, T. Amano, S. Takano, T. Kori, T. Yamazaki, and Y. Kimishima, Physica C 140, 6 (2006).
[28] A. A. Golubov, A. Brinkman, O. V. Dolgov, J. Cortus, and O. Jepsen, Phys. Rev. B 66, 054524 (2002).
[29] R. T. Gordon, N. Hi, C. Martin, M. A. Tanatar, M. D. Vannette, H. Kim, G. D. Samolyuk, J. Schmalian, S. Nandi, A. Kreyssig, et al., Phys. Rev. Lett. 102, 127004 (2009).