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Evidence for unconventional superconductivity in the nonoxide perovskite $MgCNi_3$ from penetration depth measurements

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The London penetration depth $\lambda(T)$ was measured in polycrystalline powders of the nonoxide perovskite superconductor $MgCNi_3$ by using a sensitive tunnel-diode resonator technique. The penetration depth exhibits distinctly non *s*-wave BCS low-temperature behavior, instead showing quadratic temperature dependence, suggestive of a nodal order parameter.

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Identification of the symmetry of the order parameter in superconductors is one of the most challenging experimental problems in distinguishing conventional from unconventional superconductivity. Theoretically, there are several possibilities, including the Bardeen-Cooper-Schrieffer (BCS) *s*-wave[1] and unconventional *p*- and *d*-wave pairing scenarios.[2–5] Each particular symmetry imposes constraints on the possible mechanism of electron-electron pairing. Determination of the pairing type, however, is often difficult. Electron-doped high-T_c cuprates, for example, were thought to exhibit *s*-wave BCS behavior, and only recently were shown to be *d*-wave superconductors.[6,7] The recently discovered[9] nonoxide perovskite superconductor $MgCNi_3$ is especially important, because it is viewed as a bridge between high-T_c cuprates and conventional intermetallic superconductors. This material is close to a magnetic instability on hole doping, and it is therefore natural to ask whether an unconventional pairing mechanism might be operating.[10] The absence of good single crystals and oriented films does not allow the use of phase-sensitive techniques[11,12] to probe pairing symmetry, and therefore other methods must be employed. Thermal, magnetization, resistivity, nuclear spin-lattice relaxation, and tunneling studies of $MgCNi_3$ have been reported.[8,13–18] The low-temperature London penetration depth measurements reported here provide new insight into the nature of the superconductivity in $MgCNi_3$.

The current experimental situation is highly controversial. On one hand, evidence for conventional *s*-wave behavior is found in specific-heat measurements,[13,14] although the authors disagree on the coupling strength. The nuclear spin-lattice relaxation rate $1/^{13}CT_1$ seems to exhibit behavior characteristic of an *s*-wave superconductor.[19] Some tunneling data support conventional *s*-wave pairing.[15] On the other hand, a zero-bias conductance peak (ZBCP) attributed to Andreev bound states has been observed, and it was argued that the observed ZBCP could not be due to intergranular coupling or other spurious effects.[16] Nonmagnetic disorder introduced by irradiation was found to significantly suppress superconductivity.[17] Such suppression is not expected in materials with a fully developed gap, and is a strong indication of an order parameter with nodes. Theoretical calculations support this conclusion.[18] Furthermore, recent theoretical developments predict the possibility of a unique unconventional state,[20] which might reconcile apparently contradictory experimental observations.

Previous studies conclude that more experimental data are needed in order to draw a conclusion regarding the pairing symmetry in $MgCNi_3$. It is very difficult to experimentally identify the nonexponential contribution of low-energy quasiparticles due to the presence of nodes in the superconducting gap on the Fermi surface. In the case of thermal measurements, this electronic contribution is masked by a large phonon contribution. For electromagnetic measurements, sensitivity is typically a problem. Precise measurements of the London penetration depth are therefore very important.

In this paper we report measurements of the magnetic penetration depth $\lambda(T)$ down to 0.4 K in polycrystalline powders of the nonoxide perovskite superconductor $MgCNi_3$ ($T_c \approx 7.2$ K). The sample employed for this measurement was exactly the one of composition $MgC_{0.98}Ni_3$ characterized by neutron diffraction.[21] The synthesis is described in detail in that publication.

In order to avoid artifacts related to possible intergrain coupling, three different samples were prepared: powder mixed in paraffin, powder mixed and solidified in low-temperature Stycast 1266 epoxy, and a pellet sintered at room temperature and 2.5 GPa for 8 h. All samples showed similar low-temperature behavior, indicating no additional contribution from intergrain coupling. We note that our previous measurements of MgB_2 powder of similar grain size gave results fully consistent with *s*-wave symmetry and are in complete agreement with measurements performed on single crystals.[22] In addition, a sample cut from a polycrystalline niobium foil was measured for comparison.

The penetration depth $\lambda(T)$ was measured by using a 13 MHz tunnel-diode driven LC resonator[23,24] mounted in a ^{3}He refrigerator. An external dc magnetic field (0–6 T) could be applied parallel to the ac field (~5 mOe). The oscillator frequency shift $\Delta f = f(T) - f(T_{min})$ is proportional

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to the linear ac susceptibility and, therefore, to the change in the penetration depth, $\Delta\lambda = \lambda(T) - \lambda(T_{min})$.[24] At low temperatures, $\Delta f = -\Delta f_0 \Delta\lambda / R$, where Δf_0 is the total frequency shift when the perfectly diamagnetic sample is inserted into an empty resonator, and R is the characteristic sample size.[6,23] In the case of powders, the observed frequency shift is the sum of contributions from individual grains. The grain-size distribution obtained from scanning electron microscopy (SEM) image analysis followed log-normal distribution centered around 0.6 μm with $\sigma = 0.2$ μm. To verify that granular nature does not introduce unwanted effects, we solved numerically the London equation for the actual size distribution. The calculated response was always additive, with no noticeable interference effects. Furthermore, we solved BCS equations for integral superfluid density with our grain-size distribution and found no deviations from the exponential behavior at low temperatures. The computations were done in Matlab using Femlab multiphysics Toolbox.[24,25] An experimental approach using sensitive bulk magnetization measurements on powder superconductors was effectively employed to study penetration depth in high-T_c cuprates.[26] It has also been successfully used in tunnel-diode resonator measurements of MgB_2 powders[22] and polycrystalline wires.[27] Using the approach described in Ref. 22 we estimated $\lambda(0) \approx 2500 \pm 200$ Å in agreement with literature data.[16]

Although we can only estimate the absolute value of the magnetic penetration depth, our technique provides a very sensitive (1 part per 10^{10}) detection of the *change* in the penetration depth. By varying temperature, $\Delta\lambda(T)$ is obtained. In all plots, $\Delta f(T)/\Delta f_0$ proportional to $\Delta\lambda(T)$ through a calibration constant is shown. The calibration constant depends on grain-size distribution and the number of grains per unit volume of a composite material, and is difficult to estimate reliably. Importantly, it does not influence the temperature variation, which is the focus of this work.

Clear evidence for a *d*-wave superconducting order parameter is linear temperature variation of the London penetration depth, $\Delta\lambda(T)/\lambda(0) \approx \ln 2/\Delta(0)T$.[3,5] In a conventional *s*-wave superconductor, on the other hand, an exponential decay is expected for the penetration depth: $\Delta\lambda = \lambda(0)\sqrt{\pi\Delta(0)/2T}\exp(-\Delta(0)/T)$ for $T \lesssim 0.32T_c$ with $\Delta(0)/T_c = 1.76$.[2,3] Measurements on a nonoriented powder mean that the result is averaged over all contributions $\lambda_{a,b,c}$. Fortunately, $MgCNi_3$ is isotropic and therefore we obtain values characteristic for this material.

Figure 1 presents $\lambda(T)$ measured in $MgCNi_3$ powder mixed in paraffin. The data are compared with the measurements performed on a sample cut from a polycrystalline niobium foil. The niobium data are fully consistent with the weak coupling *s*-wave BCS picture (in the entire temperature range). The data for $MgCNi_3$ also approach saturation on decreasing temperature. The magnetization measured on a commercial magnetometer would show no temperature dependence in the low-temperature region. However, our resolution is sufficient to study the low-temperature part. Apparently, the data obtained for $MgCNi_3$ are strikingly different from that of Nb. The inset in Fig. 1 shows actual penetration depth values.

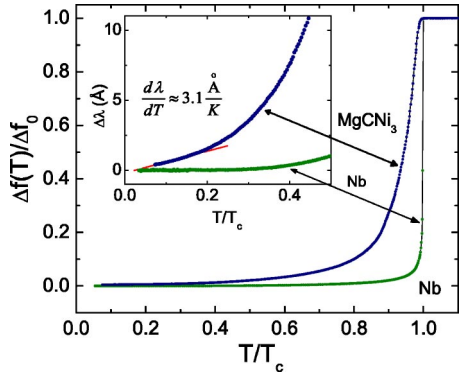

FIG. 1. Magnetic penetration depth measured in zero external field in $MgCNi_3$ (upper curves) compared to polycrystalline Nb foil (lower curves). The inset shows actual penetration depth at low temperatures.

Although the observed temperature dependence is obviously not exponential, it is instructive to attempt to fit the data to the standard low-temperature BCS form with $\Delta(0)/T_c$ being a free parameter. Figure 2 shows such a best fit, which clearly does not describe the data. In addition, the extracted $\Delta(0)/T_c = 0.83 \pm 0.02$ is too low. The inset shows the residual, $Data - Fit$, which reveals large systematic deviation from the BCS behavior down to the lowest temperature.

The measured temperature dependence of $\Delta\lambda(T)$ is plotted versus T^2 in Fig. 3. The observed behavior is quite linear on this T^2 scale up to $T/T_c \approx 0.25$. The inset shows the residuals plot, which confirms an overall good agreement of the fit with the experimental data. The residuals plot scales in the insets of Figs. 2 and 3 have the same absolute ordinate scale for easy visual comparison, showing the dramatically better power-law fit to the data. A fit to the power-law dependence, $\lambda(T) \sim T^n$ with the exponent n as a free parameter

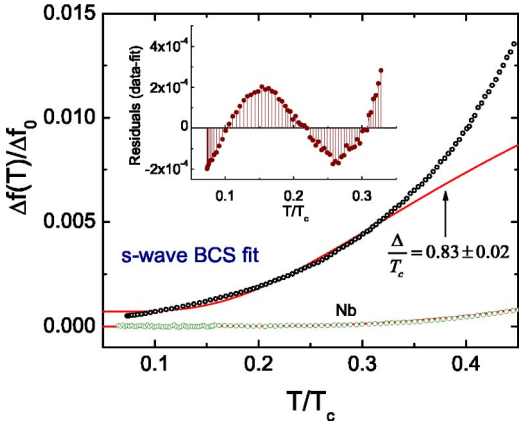

FIG. 2. Upper curve: Best *s*-wave BCS fit for $MgCNi_3$ using a standard expression (described in the text) with $\Delta(0)/T_c$ as a free parameter. The lower curve shows Nb sample and a standard BCS fit. Inset: residuals, $Data - Fit$, for the best *s*-wave BCS fit, which yields $\Delta(0)/T_c = 0.83 \pm 0.02$.

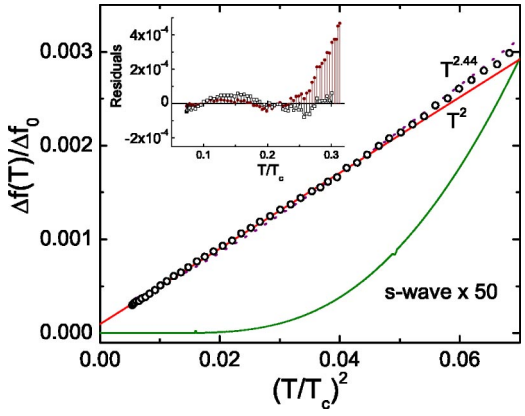

FIG. 3. Penetration depth plotted versus T^2 compared to a standard *s*-wave curve. The fit to a pure T^2 behavior is shown by solid line. The fit to T^n with *n* as a free parameter is shown by dotted line. Inset: residuals for fit with $n=2$ (solid symbols) compared to the residuals of $n=2.44$ fit. The vertical scale of the inset is the same as in the inset of Fig. 2 for comparison.

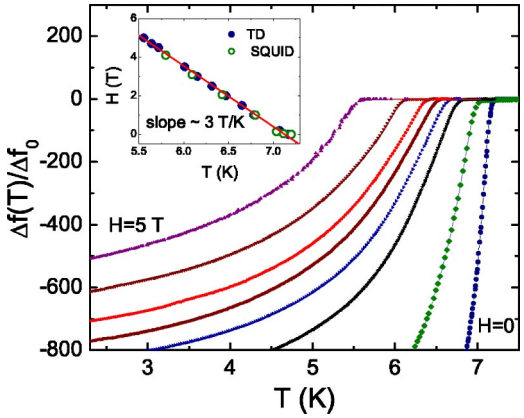

FIG. 4. $\lambda(T)$ measured at different values of the external dc magnetic field, from $H=0$ to $H=5$ T. The inset shows onset of superconductivity in tunnel diode measurements (closed symbols) compared to superconducting quantum interference device (SQUID) magnetometer measurements (open symbols).

is also shown in Fig. 3. The best fit gives $n\approx 2.44$, however, this is fit-range dependent. The obtained values of *n* decrease upon reduction of the fit-range and approach $n=2$ below $T/T_c\approx 0.25$, which is another indication of the robustness of the inferred $\lambda(T)\sim T^n$ behavior. The residuals of the $n=2.44$ fit are compared to the $n=2$ residuals in the inset to Fig. 2.

In a clean *d*-wave superconductor, a linear temperature dependence of $\Delta\lambda(T)/\lambda(0)=T\ln 2/\Delta(0)$ is predicted[3,5] and observed.[28] However, this behavior is not expected in our case of microcrystalline powder with natural grain surface roughness. In such a case, temperature dependence resulting from impurity scattering provides a more plausible model, where a quadratic temperature variation of $\Delta\lambda(T)$ is expected.[3,5,28] The rate of change is $d\lambda/dT\approx 3.1$ Å/K, comparable to 4–5 Å/K observed in yttrium barium copper oxide (YBCO).[28] Indeed, if we had pure linear variation of $\lambda(T)$, the rate of change would be somewhat larger. There is an alternative explanation for T^2 behavior in a *d*-wave superconductor. The divergence of the effective coherence length $\xi=h v_F/\pi\Delta(\mathbf{k})$ (where v_F is the Fermi velocity) near the nodes of a *d*-wave order parameter yields $\Delta\lambda(T)\sim T^2$ due to nonlocal electrodynamics.[29] Nonlocality is predicted to arise below $T_{nonlocal}\approx\xi(0)\Delta(0)/\lambda(0)$, where $\xi(0)$ is the coherence length at zero temperature. In $MgCNi_3$ $T_{nonlocal}\approx 0.05T/T_c$, estimated using reported superconducting parameters.[16] Since we observe quadratic temperature dependence up to roughly $T/T_c=0.25$, nonlocality is unlikely to explain the observed behavior.

Another possibility that might result in apparently non-*s*-wave behavior of $\lambda(T)$ would be to have a significant distribution of transition temperatures, T_c, due to inhomogeneities in chemical composition. However, our numerical solution in the framework of the weak-coupling *s*-wave BCS theory indicates that in order to mimic the T^2 behavior observed, the sample would have to contain a linear probability distribution of T_c's extending from 7.2 to 0 K. This kind of distribution is chemically unfeasible, and, in addition, is impossible for MgC_xNi_3 because the perovskite phase becomes chemically unstable at a minimum T_c of 2.5 K.[21] The absence of phases with T_c's below 2.5 K means that what appears to be non-BCS behavior cannot be induced in the low-temperature range of interest here by chemical inhomogeneity. Finally, there is neither indication of chemical inhomogeneity induced broadening in the neutron-diffraction pattern[21] nor in the observed superconducting transition (see Fig. 4), indicating that the observed T^2 behavior cannot have a chemical origin.

The interpretation of our data in terms of a particular superconductivity mechanism is further complicated by the fact that some reports suggest that $MgCNi_3$ is a multiband superconductor in which nontrivial interband coupling may reconcile existing *s*-wave observations with unconventional superconductivity. Calculations by Voelker and Sigrist[20] performed along these lines call for new experimental data, in particular, penetration depth measurements. We hope results reported here will motivate further theoretical study.

Figure 4 shows measurements of the penetration depth at various values of the external dc magnetic field. The overall behavior suggests weak pinning—the screening strength reduces due to a rapid increase of the Campbell penetration depth. By measuring the onset of superconductivity at different fields, the $H_{c2}(T)$ dependence can be reconstructed. The inset of Fig. 4 shows the onset temperature compared to the onset temperature obtained by using *Quantum Design* MPMS magnetometer. The good agreement is an independent evidence that our results, obtained on a 13 MHz resonator, are not introducing undesirable frequency effects. From the measurements of the upper critical field, we obtain $dH_{c2}/dT\approx 3$ T/K, which is consistent with previous measurements.[17,30]

In conclusion, we have presented measurements and detailed experimental analysis of the London penetration depth in the nonoxide perovskite superconductor $MgCNi_3$. Our results show clear evidence for the quadratic temperature variation of $\lambda(T)$ at temperatures below $\approx 0.25T_c$. This be-

havior indicates the presence of low-energy quasiparticles, and therefore unconventional non *s*-wave superconductivity. It is consistent with *d*-wave pairing in the presence of strong impurity scattering, but other unconventional mechanisms may be implied.

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