Microwave Properties of Borocarbide Superconductors $\text{LnNi}_2\text{B}_2\text{C}$

($\text{Ln} = \text{Y, Er, Tm, Ho}$)

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Abstract

We report measurements of the microwave surface impedance of the borocarbide family of superconductors $\text{LnNi}_2\text{B}_2\text{C}$ ($\text{Ln} = \text{Y, Er, Tm, Ho}$). The experiments enable direct measurements of the superfluid density, and are particularly sensitive to the influence of magnetic pairbreaking. In $\text{HoNi}_2\text{B}_2\text{C}$ the antiferromagnetic transition is clearly observed at zero field, and leads to a drastic reduction of the superfluid density, which recovers at lower temperatures. In $\text{ErNi}_2\text{B}_2\text{C}$ the antiferromagnetic transition is not seen in zero field data. Magnetic effects are responsible for anomalies in the low temperature surface impedance below approximately 4K in $\text{HoNi}_2\text{B}_2\text{C}$ and $\text{TmNi}_2\text{B}_2\text{C}$. The temperature dependence of the microwave impedance disagrees with simple BCS calculations.

Recently superconductivity was discovered in quaternary multiphase $\text{Y-Ni-B-C}$ [1], in
multiphase Y-Pd-B-C system [2] and in single phase LnNi$_2$B$_2$C (Ln=Y, Ho, Er, Tm, Lu) [3]. These materials are a class of intermetallic superconductors. While some members of the family, e.g. YNi$_2$B$_2$C, appear to show conventional superconducting behavior [4,5], other members, with Ln=Tm, Er, Ho, undergo an antiferromagnetic (AFM) transition at $T_N$, below the superconducting transition at $T_c$. Thus in addition to the important question of the nature of superconductivity issues concerning the interplay of magnetism and superconductivity arise in these materials.

Microwave measurements of superconductors yield unique information regarding the superfluid density, the quasiparticles and the nature of the pairing [6]. Despite the fact that magnetic superconductors such as ErRhB$_4$ have been known for about two decades, there have been few microwave studies of such superconductors. In this paper we report the first measurements of the microwave response of several members of the family, LnNi$_2$B$_2$C with Ln = Y, Er, Tm, Ho.

Single crystals of LnNi$_2$B$_2$C were grown out of Ni$_2$B flux. Details are provided in Ref. [5]. The crystals have a plate-like morphology and X-ray diffraction indicates that they have their crystallographic c-axis perpendicular to the surface of the plate. Powder X-ray diffraction on ground single crystals indicate that there is a small amount of Ni$_2$B flux contaminating the crystal, probably on the surface. This contamination is estimated to be below the 5% level. These crystals have been extensively characterized by a variety of techniques [5,7–9] besides the microwave studies discussed here. Polycrystalline samples of YNi$_2$B$_2$C were also prepared and measured.

Microwave measurements were carried out in a Nb cavity using a high precision “hot finger” method [10], in which the cavity is maintained at 2 K while the sample temperature is varied from 2 K to as high as 200 K. The surface resistance of the sample is obtained from measurements of the resonator Q using $R_s = \Gamma [Q_s^{-1}(T) - Q_o^{-1}(T)]$, where $Q_s$ and $Q_o$ are respectively the resonator Q’s with and without the sample. Similarly changes in the reactance are obtained from $\Delta X_s = \mu_0 \omega \Delta \lambda = (-2\Gamma/f_0) [f_s(T) - f_0(T)]$, where $f_s$ and $f_0$ represent the resonant frequency with and without the sample. To get the absolute value
of the reactance, an indeterminate constant $X_0$ needs to be added. In materials which obey the skin depth limit in the normal state, one can use the criterion that $R_n = X_n$ above $T_c$ to determine $X_0$ and so the absolute value of $X_s$. The geometric constant $\Gamma$ was calculated, and confirmed using measurements on known samples of Cu. The method has been extensively validated via measurements on a variety of samples, from conventional low temperature superconductors, to high temperature superconducting crystals and films [11].

Because we are able to measure both the real and imaginary parts of the impedance $Z_s = R_s + iX_s$, it is possible to obtain the complex conductivity $\sigma_s = \sigma_1 - i\sigma_2$ from the present measurements, using the relation $Z_s = R_n\sqrt{2i/(\sigma_s/\sigma_n)}$, where $R_n$ and $\sigma_n$ are the normal state surface resistance and conductivity respectively. Of particular importance is the imaginary part $\sigma_2$. This quantity is a measure of the superfluid density $n_s$ which is proportional to $\sigma_2$. It is also related to the penetration depth via $\sigma_2 = 1/\mu_0 \omega \lambda^2$.

The microwave resistivity $\rho_{\mu n}(T)$ in the normal state, see Fig. 1, was obtained from the surface resistance using $R_n = \sqrt{\pi \mu_0 f \rho_{\mu n}}$ where $\mu_0$ is the permeability of free space. The data is in good agreement with dc measurements [12], confirming that the classical skin-depth regime applies in the normal state.

\textbf{YNi₂B₂C}

The superconducting surface resistance $R_s(T)$ of several samples of YNi₂B₂C are shown in Fig. 2. The polycrystal shows higher $R_n$ and also a slightly broader transition than single crystals. It is evident that $R_s$ does not go to zero as $T \to 0$. Thus there is a residual surface resistance which is of the order of $10 - 20 \, m\Omega$ and is, possibly, extrinsic in origin. This residual resistance does depend on sample characteristics such as crystallinity and surface preparation, being lowest for the polished single crystal #4. This is probably due to slight flux contamination which leads to a temperature-independent microwave loss.

Fig. 2 also shows the surface reactance $X_s(T)$. The absolute value was obtained by normalizing to $X_n = R_n$ above $T_c$. A striking feature of the reactance $X_s$ data is the peak near $T_c$. This can be understood from simple models of the superconducting state such as two-fluid or BCS (see below). This is in fact occasionally observed in other superconductors, and
is due to buildup of superfluid, which leads to a situation where \( \lambda > \delta_n \), the superconducting penetration depth is bigger than the normal state skin depth. This results in a peak in \( X_s \) which we have observed in Y\(_1\)Ba\(_2\)Cu\(_3\)O\(_{1-\delta}\) \([13]\) also. If we subtract the residual resistance from the low temperature reactance we can estimate a zero-temperature penetration depth \( \lambda(0) = 1100 \text{Å} \) for sample #1. Although this method is not very sensitive to the absolute magnitudes the agreement with other estimates of \( \lambda(0) = 1200 \text{Å} \) \([5]\) is good.

**TmNi\(_2\)B\(_2\)C**

While the overall behavior of TmNi\(_2\)B\(_2\)C near and slightly below \( T_c \) is similar to the \( Y \) compound (see Fig. \([3]\), a noteworthy feature is the *increase* of \( R_s \) at low temperatures. This is due to increasing magnetic coherence which results in a AFM transition at 1.5\( K \) \([14]\), which is however just below the lower limit of our apparatus. This is also consistent with a decrease of \( H_{c2} \) observed in the same temperature region \([15]\). The data demonstrate that the microwave measurements can provide a measure of the magnetic scattering through the influence on the surface impedance of the superconducting state.

**ErNi\(_2\)B\(_2\)C**

The response of this compound appears similar to that of the \( Y \) compound as shown in Fig. \([3]\). Interestingly the AFM transition which should occur at 6.0\( K \) \([16,15]\) as observed in specific heat, dc-resistivity and magnetic susceptibility measurements, does not appear in the microwave data. Thus in this compound, the AFM transition is not accompanied by pairbreaking in zero field. There is however a weak shoulder in the \( R_s \) data at around 9.5\( K \) which is not associated with a feature in any other measurement.

**HoNi\(_2\)B\(_2\)C**

A detailed plot of \( R_s(T) \) vs. \( T \) in the region from 2\( K \) to 10\( K \) is shown in Fig. \([4]\). The drop in \( R_s \) at the superconducting transition temperature of 8\( K \) is clearly seen. In all conventional superconductors, and in YNi\(_2\)B\(_2\)C as shown above, \( R_s \) decreases monotonically from the normal state value \( R_n \). Remarkably, in HoNi\(_2\)B\(_2\)C \( R_s \) starts to increase again at around 6\( K \). This is due to pair-breaking which accompanies the development of the antiferromagnetic state. At the AFM transition, \( R_s \) shows a *peak*. Peaks in \( R_s \) are never seen in conventional
superconductors, although non-monotonic dependence has been observed in $Y_1\text{Ba}_2\text{Cu}_3\text{O}_{1-\delta}$ [17].

It is very interesting to study the reactance as a function of temperature, also shown in Fig. 4. Below the superconducting transition at $8K$, $X_s$ increases due to the buildup of superfluid, as for the other superconductors, and then starts to decrease. However the AFM transition intervenes and appears as a peak, due to pairbreaking.

At low temperatures, both $R_s$ and $X_s$ are seen to increase with decreasing $T$. Although this is similar to that observed in TmNi$_2$B$_2$C, there is no AFM transition at a comparable temperature. Thus our data indicates a possibly new source of magnetic scattering below about 3.75$K$.

**Complex Conductivity and Superfluid density**

The real and imaginary parts of the conductivity $\sigma_1$ and $\sigma_2$ of YNi$_2$B$_2$C are shown in Fig. 5. Note that a residual $R_{s,\text{res}}$ was subtracted while computing the complex conductivity. $\sigma_2$ has a “conventional” temperature dependence in that it rises smoothly at $T_c$ to a large value at low temperatures. However the detailed temperature dependence does not fit any conventional form such as $(1 - t^4)$ of the 2-fluid model or a BCS form. Instead $\sigma_2$ appears to be well described by a $(1 - t)$ temperature dependence, except for a very slight curvature. $\sigma_1$ rises from its normal state value and has a peak at around $0.5T_c$. This is not the behavior expected from BCS coherence factors since there the peak is around $0.9T_c$. Instead this is similar to the behavior of $\sigma_1$ of YBa$_2$Cu$_3$O$_{7-\delta}$ where there is a peak at around $0.4T_c$ [17].

In HoNi$_2$B$_2$C, $\sigma_2$ and hence $n_s$ are found to initially increase (see Fig. 4). However the AFM transition arrests this increase, and reduces the superfluid density, although superconductivity is not completely destroyed since $\sigma_2$ does not become zero. Below the AFM transition, $\sigma_2$ recovers. It is interesting that the behavior of $\sigma_2$ very closely mirrors that of $H_{c2}$ [9]. The AFM transition is also reflected in the temperature dependence of $\sigma_1$.

**Discussion and Comparison with Theory**

In order to address the issue of the nature of the superconducting order parameter, we plot the normalized surface resistance $(R_s(T) - R_{s,\text{res}})/R_s(T_c)$ vs. $t = T/T_c$ for all the
superconductors that were measured. The resulting plot shown in Fig. 6 is noteworthy in that the scaled plot appears to indicate a common, underlying temperature dependence, independent of sample, except of course for the expected deviations near $T_N$ in HoNi$_2$B$_2$C and the low temperature rise for HoNi$_2$B$_2$C and TmNi$_2$B$_2$C. Also shown in Fig. 6 is a comparison with numerical calculations based on the BCS theory using a Mattis-Bardeen complex conductivity in the local limit \cite{18}. The gap parameter $\Delta(0)/kT_c$ was used as an input parameter. The data do not agree with the numerical calculations if the mean-field value $\Delta(0)/kT_c = 1.74$ is used. Instead a much lower value 0.49 fits the data better. This appears to be in conflict with measurements which suggest a BCS s-wave state for the borocarbides. Indeed gap ratios of 1.45 to 1.95 for YNi$_2$B$_2$C have been reported \cite{14,19,20}.

The data differ from the simple BCS analysis in three ways: (1) the broader temperature dependence which can be modeled as a smaller gap ratio, (2) the peaks at the AFM transition, and (3) the low temperature rise in HoNi$_2$B$_2$C and TmNi$_2$B$_2$C. The latter two features can be attributed to pair-breaking by the magnetic constituents Ho and Tm. While the first feature could arise from sample inhomogeneities at the surface, an interesting question is whether the broadened transition could be due to an unidentified source of pairbreaking which should then be present in all the compounds. Equally noteworthy is the absence of any signature of the AFM transition in the $Er$ superconductor. Neutron scattering studies of HoNi$_2$B$_2$C \cite{7} have shown the existence of a modulated magnetic structure from 6 K to about 4.7 K. Similar features are not observed in ErNi$_2$B$_2$C \cite{21,22}. Pairbreaking is significant only when there exists magnetic fields over length scales comparable to the coherence length, and this appears to occur in HoNi$_2$B$_2$C, but not in ErNi$_2$B$_2$C.

In conclusion, the microwave properties of several borocarbide superconductors reveal novel features of the superconducting state. The superfluid density which is obtained from the data displays striking features due to the influence of magnetic pairbreaking. The data reveal interesting results on the interplay of magnetism and superconductivity which deserve further experimental and theoretical studies.

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FIG. 1. Microwave resistivity of $\text{LnNi}_2\text{B}_2$ ($\text{Ln}=\text{Y, Er, Tm, Ho}$) in the normal and superconducting states extracted from the surface resistance. #1 to #4 are different $\text{YNi}_2\text{B}_2\text{C}$ single crystal samples.

FIG. 2. $R_s$ and $X_s$ of $\text{YNi}_2\text{B}_2\text{C}$ in the superconducting state for a polycrystal and single crystals (#1 and #4).
FIG. 3. $R_s$ and $X_s$ of TmNi$_2$B$_2$C and ErNi$_2$B$_2$C.

FIG. 4. $R_s$ and $X_s$ of HoNi$_2$B$_2$C. The AFM transition at 5.2 K is clearly visible.
FIG. 5. Real ($\sigma_1$) and imaginary ($\sigma_2$) parts of the complex conductivity of (left) YNi$_2$B$_2$C and (right) unpolished HoNi$_2$B$_2$C sample. $\sigma_2$ is proportional to the superfluid pair density.

FIG. 6. Normalised surface resistance of LnNi$_2$B$_2$C (Ln = Y, Tm, Er, Ho) in the superconducting states vs. reduced temperature. The residual $R_s(T \to 0)$ has been subtracted out in each case. Also shown are BCS calculations with $\Delta(0)/kT_c = 1.74$ (dashed line) and 0.45 (solid line).