Local superconducting density of states of ErNi$_2$B$_2$C

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Abstract

We present local tunnelling microscopy and spectroscopy measurements at low temperatures in single crystalline samples of the magnetic superconductor ErNi$_2$B$_2$C. The electronic local density of states shows a striking departure from s-wave BCS theory with a finite value at the Fermi level, which amounts to half of the normal phase density of states.

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During the last decade, many studies of the quaternary rare earth, nickel borocarbides have provided important insight into the intriguing and long standing problem of coexistence of magnetic and superconducting orders \[1, 2\]. In particular, compounds with RNi\(_2\)B\(_2\)C and R = Y, Lu, Tm, Er, Ho and Dy, are superconducting although their magnetic properties are very different. The compounds with R = Y and Lu bring only the superconducting character into play and have the highest critical temperatures of the series (\(T_c = 15.5 \) and 16.5 K respectively). Those with R = Tm, Er, Ho or Dy are magnetic superconductors with smaller but still sizable critical temperatures (\(T_c = 11, 10.5, 8.6 \) and 6 K respectively) \[2\]. In all of them, high quality single crystalline samples have been grown in several laboratories, and there are in addition experiments and calculations of the electronic bandstructure \[2, 3, 4, 5\]. All these circumstances have promoted a notable interest in this family, considered by many as a "toy-box" where an impressive range of new physical effects are to be found \[6\].

The compounds ErNi\(_2\)B\(_2\)C and TmNi\(_2\)B\(_2\)C have very similar \(T_c\)'s, which are the highest among the magnetic compounds of the series. Nevertheless, their magnetic properties are radically different. TmNi\(_2\)B\(_2\)C is paramagnetic down to 1.5 K, where it transits to an antiferromagnetic state with an incommensurate wavevector \[7, 8\]. The ordered magnetic moment amounts to 3.8 \(\mu_B\), and is much smaller than the one of ErNi\(_2\)B\(_2\)C (7.2 \(\mu_B\)), which transits already below \(T_N = 6\) K, to an also incommensurate spin density wave, and below \(T_{WF} = 2.3\) K to a peculiar weak ferromagnetic state where one of each twenty Er spins are aligned resulting in a small net magnetic moment of 0.33\(\mu_B\) per Er atom \[9, 10, 11, 12, 13, 14, 15\]. Several remarkable new effects have been found to occur below \(T_{WF}\) as a consequence of weak ferromagnetism. For instance, the vortex lattice tilting away by a small but measurable amount (up to 1.6 degrees) from a magnetic field applied perpendicular to the magnetic moments, i.e. in the plane of the tetragonal crystal structure \[16\], or an increase of the critical current \[17\]. There are however no available data of the electronic excitation spectrum. Here we present measurements of the superconducting electronic density of states using local tunnelling spectroscopy. We find that ErNi\(_2\)B\(_2\)C exhibits yet another interesting property, absent in other nickel borocarbide compounds, namely an anomalously high amount of low lying electronic excitations in the local density of states.

We use a very similar STM set-up as in previous measurements in other superconducting nickel borocarbide materials (TmNi\(_2\)B\(_2\)C \[18\], and the non-magnetic YNi\(_2\)B\(_2\)C, LuNi\(_2\)B\(_2\)C with \(T_c = 15.5\) K and 16.5 K \[19\]). The spectral resolution of the experimental set-up has
FIG. 1: In a. we show several characteristic tunnelling spectra, taken at 0.15 K, and shifted by +0.18 (tunnelling resistance \( R_T = 10 \, \text{M}\Omega \)). In the insets we show typical topography (left) and STS (right) images found in ErNi\(_2\)B\(_2\)C. The full range in contrast from black to white represents, respectively, a height difference of 20 nm in topography (left) and a change in the zero bias conductance of 20% in STS (right). Crosses and numbers give points where the tunnelling spectra shown in the figure (top) were obtained. For comparison we show in b. data of the similar material TmNi\(_2\)B\(_2\)C, published in [18], and taken at 0.8 K.

been improved through the measurement of low critical temperature superconductors as Al and PrOs\(_4\)Sb\(_{12}\) (\( T_c = 1.12 \, \text{K} \) and 1.85 K respectively), where we were able to obtain clean spectra with a negligible conductance at zero bias and a resolution in energy of 15 \( \mu \text{eV} \) [20, 21]. In addition, we have added a blade to the sample holder, so that the samples can be broken in-situ, at low temperatures under cryogenic ultra high vacuum. We mount small (about 1x1x5 mm\(^3\)) single crystalline samples into the sample holder. After cooling, we break the samples with the blade and approach a clean gold tip mounted on a piezotube with a scanning range of 600x600 nm\(^2\). An x-y table permits macroscopic positioning of the tip over the sample and allows to study scanning windows in macroscopically different regions of each sample, without heating the whole set-up. As demonstrated in all other
previous STM studies made in the borocarbides by us and other groups\cite{18, 19, 22, 23}, the samples show a conchoidal fracture, without a clear cleaving plane. Accordingly, the surface of these samples, as measured with the STM, has large relatively flat regions, showing at the smallest scales a small but finite roughness \cite{18, 19, 22, 23}. Therefore, tunnelling is typically made at arbitrary directions, so that it becomes especially important to study a large number of samples in macroscopically different regions. We successfully broke in-situ fourteen samples, verifying after the measurements the good quality of the surfaces with a SEM, and the tunnelling plane using X-ray scattering. Surfaces in and out of plane, as well as in intermediate directions have been probed. In each sample, we studied between five and ten different scanning windows. We took current-voltage curves in different positions, and also studied systematically scanning tunnelling spectroscopy images (STS), obtained by making a current-voltage curve at each point of a 64x64 array, and subtracting the conductance well within the quasiparticle peaks from the conductance at high bias (see for more details Refs. \cite{18, 19, 22, 23}). In all cases, we found surfaces of high quality, as in previous work, but with dramatically different tunnelling spectra for the case of ErNi$_2$B$_2$C, as will now be discussed.

At the lowest temperatures, tunnelling spectra as shown in Fig. 1a are always found over large areas of the surface. These curves differ radically from the predictions of s-wave BCS theory. Instead of a wide energy range with a zero conductance, we find a finite conductance at zero and low bias, which corresponds to about one half of the high bias conductance. We have included in Fig. 1b the spectra obtained in the very similar superconductor TmNi$_2$B$_2$C, published in Ref.\cite{18}. In TmNi$_2$B$_2$C, the form of the spectra follow the BCS, s-wave theory quite closely with a negligible conductance at the Fermi level. In the non-magnetic compounds YNi$_2$B$_2$C and LuNi$_2$B$_2$C, we also always find a negligible conductance at the Fermi level \cite{19}.

In Fig. 1a we show a typical STS image (bottom right), which represents the changes found in the zero bias conductance in the 400 x 400 nm$^2$ window whose topography is represented in the bottom left image of Fig. 1a. Clearly, the spectra remain with the same form in the whole scanning range, apart small variations of 10-20% (grey scale in bottom right image of Fig. 1a), which are not correlated to any patterns in the topography. Similar images and spectra have been found in all fourteen in-situ broken single crystalline samples.

At temperatures much below T$_c$, the local tunnelling conductance is a direct measure
of the local density of states $N_{\text{loc}}(E)$. Its form depends on the superconducting properties of the surface, its detailed electronic structure, and on the tunnelling plane. Our experiment evidences a high density of states at the Fermi level together with a well defined V-shaped increase between zero bias and the peak observed at $\Delta = 1.8$ meV (Fig. 1a). This value is similar, although slightly larger, to the gap expected from most simple BCS theory ($\Delta_0 = 1.73k_BT_c$), which amounts to 1.65 meV, and to the value found in TmNi$_2$B$_2$C (1.45 meV) [18].

The temperature dependence of the superconducting spectra has been also followed making temperature scans in each sample in different positions. The changes in the tunnelling conductance when increasing temperature are shown in a representative scan in Fig. 2. The form of the local density of states is simply smeared out by temperature. The position of the peak in the local density of states $\Delta$ can be followed as a function of temperature by de-convoluting the density of states from the tunnelling conductance. It is interesting to note that, as shown in Fig. 3, the temperature variation of $\Delta$ follows well BCS prediction for the superconducting gap.

Therefore, our result evidences the presence of an important amount of ungapped excitations on the surface, which shows no sample nor orientational dependence within our experimental resolution, and of gapped excitations. The latter have a distribution of values of the superconducting gap, which produce a V-shaped density of states, and have a maximum value, $\Delta$ that decreases with temperature following BCS theory.

Clearly, the onset of magnetic order in ErNi$_2$B$_2$C at $T_N = 6$ K and $T_W = 2.3$ K does not greatly change the local tunnelling conductance. It is interesting to compare to TmNi$_2$B$_2$C, where no changes are found in the tunnelling spectra when crossing $T_N = 1.5$ K. In the antiferromagnetic phase, the local magnetic field indeed averages to zero in distances much shorter than the superconducting coherence length, as $\xi_0 = 12$ nm [24], whereas the magnetic moment changes sign approximately each 2 nm [25]. As a consequence, the superconducting density of states does not appear to be influenced by the onset of magnetic order and follows well expectations from simple BCS theory [18]. In ErNi$_2$B$_2$C, the superconducting coherence length is of the same magnitude ($\xi_0 = 13.5$ nm), and the antiferromagnetic modulation of the magnetic moment occurs at an even smaller length scale, within the unit cell [9, 10]. So that we should not expect a strong change of the superconducting density of states of ErNi$_2$B$_2$C at $T_N$ due to the local magnetic field. Nevertheless, we should point out that $T_N$
FIG. 2: The figure shows a representative temperature scan. The spectra maintain its form in the whole temperature range, without showing important changes at the magnetic transitions ($T_N = 6$ K and $T_{WF} = 2.3$ K).

is rather high in ErNi$_2$B$_2$C, well above $T_c/2$, so that the temperature induced smearing in the tunnelling conductance is significant and the determination of the local density of states is not as precise as at lower temperatures. In our experiment, at 6 K, we cannot resolve the density of states within the quasiparticle peaks better than about 30%. An effect which may produce only small changes in the local density of states and fall within this error bar is the small gap which certainly opens at the Fermi level at $T_N$ in ErNi$_2$B$_2$C, because the magnetic ordering wavevector of ErNi$_2$B$_2$C nests a small part of the Fermi surface [3, 9].

As regards the peculiar weak ferromagnetic order of ErNi$_2$B$_2$C, it is expected to create a finite magnetic field below $T_{WF} = 2.3$ K. Estimates give values which are rather small, of the same order or slightly larger than $H_{c1}$ (between 0.05 T and 0.1 T [10, 17, 26, 27]) and cannot be expected to produce changes greater than 10% on the amount of low energy excitations through magnetic pair breaking [28]. On the other hand, the possible appearance of an intriguing vortex lattice at zero field due to this small magnetic field has been discussed by several authors [26, 27]. Clearly, it does not show up on surface scanning tunnelling
FIG. 3: The position in energy of the quasiparticle peaks in the density of states, \( \Delta \), is plotted as a function of temperature. Solid line is the temperature variation of the superconducting energy gap within BCS theory. In the inset we show an example of the superconducting density of states at three different temperatures, obtained by de-convoluting the density of states from tunnelling conductance spectra. \( \Delta \) is obtained as schematically shown by the arrows.

Note that in all cases, we did follow the superconducting spectra up to the bulk \( T_c \). This rules out simple impurity pair breaking effects as the origin of the low energy excitations. In principle, pair breaking due to impurities or defects is especially significant in antiferromagnetic superconductors, where Anderson’s theorem is violated and even non-magnetic impurities act as pair breakers \[1, 29\]. However, \( T_c \) is greater than \( T_N \) in ErNi\(_2\)B\(_2\)C. Moreover, pair breaking is always associated to a decrease of \( T_c \) related to the amount of excitations created through pair breaking within the gap, which increases the zero bias conductance \[1, 29\]. Therefore, this can be fully ruled out in ErNi\(_2\)B\(_2\)C where the form of the tunnelling conductance is not sample dependent and, what is more important, survives up to the bulk \( T_c \) in all measured samples.

On the other hand, the suppression of \( T_c \) by intrinisic magnetic pair breaking due to the local moment of the rare earth has been largely discussed to explain the overall behavior of \( T_c \) along the RNi\(_2\)B\(_2\)C series \[2\]. Actually, the decrease of \( T_c \) roughly scales with the deGennes factor when going through \( R = \text{Lu, Tm, Er, Ho and Dy} \). This has been taken as an evidence for the presence of a magnetic pair breaking effect that reduces \( T_c \) along the series, following Abrikosov-Gorkov theory \[2\]. However, it does not explain the spectacular difference between
the tunnelling spectra in ErNi$_2$B$_2$C and TmNi$_2$B$_2$C. They have very different magnetic properties, but still they are adjacent compounds on the RNi$_2$B$_2$C series, located closest to the non-magnetic cases. Clearly, a more precise description, taking into account the peculiarities of each compound should be very helpful. For instance, the multiband structure of the Fermi surface, common to the whole series, has not been theoretically fully taken into account to explain the behavior of the magnetic compounds. Actually, our results can be naturally explained if the superconducting gap does not open on the whole Fermi surface of ErNi$_2$B$_2$C, but only on a fraction representing roughly half of the overall area. This would lead to the tunnelling spectra discussed here. It should be interesting to study also compounds with R = Ho and Dy as they may show even more extreme behaviors.

It is important to remember that local tunnelling spectroscopy is a surface sensitive technique. We have measured fourteen high quality single crystalline samples, prepared in the same manner as previously measured samples of RNi$_2$B$_2$C by our group (R=Y, Lu, Tm, 18,19), in the best possible conditions, i.e. fresh surfaces broken in-situ in cryogenic vacuum conditions, and in an experimental set-up with high resolution in energy that has given radically different results for R = Y, Lu, Tm. In addition, all past high resolution scanning tunnelling spectroscopy measurements made in superconductors of coherence lengths of the order of 10 nm or larger have given results that are indeed dominated by the bulk properties (see e.g. 18,19,20,21,31,32,33). So there is no a priori reason to think that the surface may be at the origin of the observed behavior. But on the other hand, present knowledge about surface magnetism in compounds with large exchange field (in comparison to TmNi$_2$B$_2$C) is very poor. Therefore, there is no way to completely rule out some surface effect related to magnetism, which would make ErNi$_2$B$_2$C a different case among the superconductors studied so far with STM. For instance, if a small ferromagnetic layer nucleates on the surface below a temperature of the order of T$_c$ or higher, it could create a sizable local magnetic field, which affects the superconducting properties at the surface. Another interesting effect, which creates a high zero bias conductance in the superconducting tunnelling density of states due to enhanced magnetic scattering near the surface, has been recently considered in Refs. 34,35. This needs to be explored in more detail and is particularly important in view of planning phase sensitive experiments in magnetic superconductors 36,37, which need typically junctions that should be very sensitive to surface magnetism.
Summarizing, we have made local scanning tunnelling spectroscopy measurements on the surface of the rare earth nickel borocarbide ErNi$_2$B$_2$C, where superconductivity coexists with weak ferromagnetism, antiferromagnetism and local moment paramagnetism when increasing temperature up to $T_c$. We directly observe a finite density of states at the Fermi level as high as half the normal state value over large areas of the surface.

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