The vast majority of known superconductors are characterized by an order parameter with \( s \)-wave symmetry and a gap function which is largely isotropic and without nodes (zeros). Only four families of materials are seriously thought to exhibit a superconducting state with such a gap function: (1) heavy-fermion materials, such as UPt\(_3\), where a line of nodes in the gap function has clearly been identified \([1]\); (2) high-\( T_c \) \( \text{cuprates} \), such as YBa\(_2\)Cu\(_3\)O\(_y\), where the order parameter was clearly shown to have \( d \)-wave symmetry \([2]\); (3) the ruthenate \( \text{Sr}_2\text{RuO}_4 \), where there is strong evidence for a triplet order parameter \([3]\); and (4) organic conductors, such as \( \kappa \)-(ET)\(_2\)Cu[N(CN)\(_2\)]Cl where there is growing evidence for unconventional superconductivity \([4]\). A major outstanding question is the nature of the microscopic mechanism responsible for superconductivity in any of these materials. The unconventional symmetry of the order parameter is evidence for a pairing caused by purely electronic interactions and not mediated by phonons. For example, the proximity to magnetic order which is found in all four families of superconductors has led to the suggestion that spin fluctuations are responsible for Cooper pairing, as is thought to be the case in superfluid \(^3\)He.

The presence of nodes in the gap function is generally associated with unconventional (non-\( s \)-wave) symmetries. These nodes are typically inferred from the observation of quasiparticle excitations at energies much lower than the gap maximum \( \Delta_0 \), as reflected, for example, in the power law temperature dependence of various physical properties, such as London penetration depth and ultrasonic attenuation at \( T \ll T_c \). Another way of detecting low-energy quasiparticles is to excite them by applying a magnetic field which introduces vortices in the material, so that the superfluid flow around each vortex Doppler shifts the quasiparticle energy. In certain limits, the quasiparticle response is the same whether induced by a thermal energy \( k_BT \) or by a field energy \( \Delta_0 \sqrt{B/B_{c2}} \), where \( B_{c2} \approx H_{c2} \), the upper critical field \([5]\).

In this Letter, we turn our attention to another class of superconductors: the borocarbides \( \text{LuNi}_2\text{B}_2\text{C} \) (where \( L = Y, \text{Lu, Tm, Er, Ho, and Dy} \) \([6]\). It has generally been thought that these materials are described by an order parameter with \( s \)-wave symmetry and pairing which proceeds via the electron-phonon coupling \([7–9]\). However, there is recent evidence for low-energy excitations in the superconducting state, whether from the anomalous field dependence of the specific heat \([10,11]\) and the microwave surface impedance \([11,12]\), or from the presence of scattering below the gap in Raman measurements \([13]\). This has been interpreted in terms of an anisotropic \( s \)-wave gap \([10,11]\) (see also Ref. \([14]\)].

Here we present compelling evidence that the gap function of \( \text{LuNi}_2\text{B}_2\text{C} \) is highly anisotropic, with a gap minimum \( \Delta_{\text{min}} \) at least 10 times smaller than the gap maximum, \( \Delta_{\text{min}} \leq \Delta_0/10 \), and possibly going to zero at nodes. This statement is based on the observation of delocalized quasiparticles at very low energies, as measured directly by heat transport. Indeed, quasiparticle conduction is induced by a magnetic field as low as \( H_{c1} = H_{c2}/100 \) and it grows linearly with field, in dramatic contrast with the exponentially activated transport seen in Nb, for example, where it results from tunneling between the localized states bound to the core of adjacent vortices. Such pronounced anisotropy challenges the current view on the nature of superconductivity in borocarbides. It suggests either a new family of unconventional superconductors (with symmetry-imposed nodes in the gap function) or \( s \)-wave superconductors with more anisotropy than has ever been seen before. In either case, the role of phonons as a proposed pairing mechanism may have to be critically reexamined.

\( \text{LuNi}_2\text{B}_2\text{C} \) is an extreme type-II superconductor and a nonmagnetic member of the borocarbide family with a superconducting transition temperature \( T_c \approx 16 \) K and an upper critical field \( H_{c2}(0) \approx 7 \) T. Its thermal conductivity \( \kappa \) was measured in a dilution refrigerator using a standard steady-state technique. A heater and two \( \text{RuO}_2 \)
thermometers were used for the measurements. The latter were calibrated in situ for each field against a germanium thermometer. The temperature was increased at fixed magnetic field, from 70 mK up, in fields ranging from 0 to 8 T. The field was applied parallel to the c axis of the tetragonal crystal structure ([001]), and perpendicular to the heat current (along [100]). Below 1.5 T, the sample was cooled in the field to ensure a good field homogeneity. Above 1.5 T, the results were independent of the cooling procedure. The single crystal was grown by a melting flux method [6]. The sample was a rectangular parallelepiped of width 0.495 mm (along [001]) and thickness 0.233 mm (along [010]), with a 1.59 mm separation between contacts (along [100]).

In zero magnetic field, \( \rho(300 \, \text{K}) = 35 \, \mu\Omega \, \text{cm} \) and \( \rho_0 = 1.30 \, \mu\Omega \, \text{cm} \), from a fit to \( \rho = \rho_0 + AT^2 \) between \( T_c \) and 50 K. There is a positive magnetoresistance such that \( \rho(8 \, \text{T}) = 1.67 \, \mu\Omega \, \text{cm} \) at \( T \rightarrow 0 \). The zero-temperature coherence length \( \xi_0 = 70 \, \text{Å} \), using \( H_{c2}(0)/4\pi \xi_0^2 \). The zero-temperature penetration depth is \( \lambda_0 = 760 \, \text{Å} \) [15]. The mean free path is approximately 500 Å. We measured the lower critical field \( H_{c1}(0) \) to be 60 mT, using the sudden drop in \( \kappa(H) \) vs \( H \) at 2 K, caused by the strong scattering of phonons by vortices as they first enter the sample.

The thermal conductivity \( \kappa(T) \) of LuNi$_2$B$_2$C is plotted in Fig. 1, as \( \kappa/T \) vs \( T^2 \). The total conductivity is the sum of an electronic and a phononic contribution: \( \kappa = \kappa_e + \kappa_{\text{ph}} \). By plotting the data in this way, one can easily separate the electronic term linear in \( T \) from the phononic term cubic in \( T \). As the temperature is decreased, and in the absence of strong electron-phonon scattering (i.e., at \( H = 0 \)), the phonon mean free path eventually grows to reach the size of the crystal, at which point \( \kappa_{\text{ph}} \sim T^3 \). The low-field curves (in the lower panel of Fig. 1) are indeed roughly linear (and parallel) in such a plot, with a slope in quantitative agreement with the known sound velocities and sample dimensions, as reported earlier [16]. At higher field, roughly above 2 T and all the way into the normal state, the conduction is essentially entirely due to electrons and given by a constant \( \kappa/T \). Note that the magnitude of this linear \( \kappa \) is in perfect agreement with the Wiedemann-Franz law, namely \( \kappa_e/T = L_0/\rho \), where \( L_0 = (\pi^2/3)(k_B/e)^2 = 2.45 \times 10^{-8} \, \text{W} \, \text{K}^{-2} \) and \( \rho = \rho(8 \, \text{T}) \). Given this well-understood behavior of \( \kappa_e(T) \) and \( \kappa_{\text{ph}}(T) \), it is straightforward to extract the electronic contribution \( \kappa_e(T) \), by simply extrapolating \( \kappa/T \) to \( T = 0 \). The result of this extrapolation is plotted as \( \kappa_e/T \) vs \( H \) in Figs. 2 and 3, where the field is normalized to unity at \( H_{c2}(0) \) and the conductivity, to its normal state value. One immediately notices the large amount of delocalized quasi-particles throughout the vortex state of LuNi$_2$B$_2$C. [This would seem to provide a natural explanation for the observation of de Haas–van Alphen oscillations down to unusually low fields (\( H_{c2}/5 \)) in YNi$_2$B$_2$C [17], a close cousin of LuNi$_2$B$_2$C, with \( T_c = 15.5 \, \text{K} \) and \( H_{c2} = 6.5 \, \text{T} \).]

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![FIG. 1. Temperature dependence of thermal conductivity at several applied fields, plotted as \( \kappa/T \) vs \( T^2 \), for (a) \( H = 0 \), 0.3, 1.5, 4, 6, and 8 T; and (b) \( H = 0 \), 50, 75, 100, 200, and 300 mT, in increasing order. The solid line indicates the value expected from the Wiedemann-Franz law above \( H_{c2} \).](image)

![FIG. 2. Magnetic field dependence of the electronic thermal conductivity \( \kappa_e/T \) at \( T \rightarrow 0 \), normalized to its value at \( H_{c2} \). Circles are for LuNi$_2$B$_2$C, squares for UPt$_3$ [23], and diamonds for Nb [18]. Note the qualitative difference between the activated conductivity of \( s \)-wave superconductor Nb and the roughly linear growth seen in UPt$_3$, a superconductor with a line of nodes. The lines are a guide to the eye.](image)
fact, the growth of quasiparticle conduction starts right at $H_{c1}$ and is seen to be roughly linear in field. This is in dramatic contrast with the behavior of quasiparticles in $s$-wave superconductors with a large finite gap for all directions of electron motion. For comparison, we show in Fig. 2 the electronic conductivity of Nb measured at 2 K (i.e., 0.22T$_c$) [18]. In an isotropic $s$-wave superconductor, the only quasiparticle states present at $T \ll T_c$ are those associated with vortices. When vortices are far apart, these states are bound to the vortex core and are therefore localized, and unable to transport heat. They thus contribute to the specific heat but not to the thermal conductivity. As the field is increased and the vortices are brought closer together, tunneling between states on adjacent vortices will cause some delocalization. This conduction is expected to grow exponentially with the ratio of intervortex separation to vortex core size ($\approx \xi_0$), namely as $\exp(-\alpha \sqrt{H_{c2}/H})$, where $\alpha$ is a constant, as is found for Nb at fields below $H_{c2}/3$ [19].

In the presence of nodes in the gap, the dominant mechanism for quasiparticle transport in the vortex state is totally different. Conduction results from the population of extended quasiparticle states in the bulk of the sample, outside the vortex cores. The excitation of these quasiparticles proceeds via the Doppler shift of their energies as they move in the presence of the superfluid flow circulating around each vortex. Because near the nodes such states exist down to zero energy, the growth in the zero-energy quasiparticle density of states starts right at $H_{c1}$, with a characteristic $\sqrt{H}$ dependence [20]. This leads to a $\sqrt{H}$ dependence of the specific heat at low temperature, as observed, for example, in the cuprate superconductor YBa$_2$Cu$_3$O$_7$ [21].

Note that the same mechanism will operate for an anisotropic $s$-wave gap if the field is such that the Doppler shift exceeds the minimum gap in the quasiparticle spectrum. It is worth noting, however, that a similar field dependence has also been observed in $s$-wave superconductors, such as NbSe$_2$ [22] where it has been attributed to the bound states in the vortex core. Specific heat studies are therefore unable to distinguish between a $\sqrt{H}$ contribution coming from localized core states and that coming from extended states outside the core. In contrast, thermal conductivity is selective, in that it probes only the contribution of delocalized excitations.

The effect of vortices on quasiparticle transport in an unconventional superconductor with a line of nodes in the gap function was studied in beautiful detail by Sudarow and co-workers [23]. Their measurements of $\kappa(T, H)$ in UPt$_3$ yield a roughly linear increase of $\kappa_c/T$ at $T \rightarrow 0$ with $H$, shown in Figs. 2 and 3. The data are for a heat current in the basal plane of the hexagonal crystal structure, which probes the equatorial line node in the gap function of UPt$_3$, established by transverse ultrasound attenuation [24]. Figures 2 and 3 reveal that quasiparticle conduction in the basal plane of LuNi$_2$B$_2$C is as good as in UPt$_3$ (or even better). At low fields, the growth in the residual linear term $\kappa_0/T = (\kappa/T)_{T \rightarrow 0}$ is also linear in $H$, starting at $H_{c1}$:

$$\frac{\kappa_0}{T} = \frac{L_0}{\rho_0} \frac{H - H_{c1}}{H_{c2}},$$

where $\rho_0$ is the zero-field normal-state resistivity. This is vastly more conductive than a typical $s$-wave superconductor. For example, electronic conduction in V$_3$Si, an extreme type-II $s$-wave superconductor with comparable $T_c$ (16.5 K) and $\xi_0$ (45 Å), is 20 times weaker at $H = 0.05H_{c2}$, as seen from data shown in Fig. 3.

In both LuNi$_2$B$_2$C and UPt$_3$, the thermal conductivity is roughly linear in $H$ and the heat capacity follows approximately a $\sqrt{H}$ dependence. The latter is naturally understood in terms of a density of states which is linear in energy (coming from nodes or minima). However, a theory that can successfully account for the linear field dependence of $\kappa_c/T$ has not yet been formulated.

Nohara et al. [10] and Izawa et al. [11] have recently attributed the $\sqrt{H}$ dependence of the specific heat they observe in YNi$_2$B$_2$C to a Doppler shift of the quasiparticle spectrum as in a $d$-wave superconductor [25] but applied in this case to a highly anisotropic $s$-wave gap, with a small minimum gap $\Delta_{min}$. Interpreting the thermal conductivity data in the same way yields an estimate of $\Delta_{min}$. Indeed, because quasiparticle conduction starts right at $H_{c1}$, the minimum gap must be smaller than the Doppler shift energy $E_D$ at $H_{c1}$. In a superconductor with a line of nodes in the gap, the average $E_D$ is given by $\approx \Delta_{min} \sqrt{B/B_{c2}}$ [25].

![Graph](image_url)
where $B$ is the magnetic field inside the superconductor and $B_2 = H_c$. At $H_{c1}$, $B = 0$ in a type II superconductor, thus possibly implying a true zero in the gap. A conservative upper bound on the minimum field required to excite quasiparticles above $\Delta_{\text{min}}$ uses $B = H_{c1}$. This gives

$$\Delta_{\text{min}} \leq E_H(H_{c1}) = \Delta_0 \sqrt{H_{c1}/H_c} \approx \Delta_0/10.$$  \hspace{1cm} (2)

In other words, there is a huge gap anisotropy, with a minimum in the basal plane (the direction of heat current).

A factor of 10 in gap anisotropy is unprecedented for an $s$-wave superconductor, with a factor of 2 being the most that has ever been inferred in elemental superconductors [26]. Faced with this striking result, two questions arise: (1) Does the gap function have $s$-wave symmetry (with deep minima) or rather another symmetry (with actual nodes)? (2) Is the pairing indeed due to phonons?

In relation to the first question, we stress that no sizable residual linear term $\kappa_0/T$ is observed in $H = 0$ (see [16]), a fact which would tend to argue against the presence of nodes in the superconducting gap. However, this may be a question of magnitude. In the cuprates, a value of $\kappa_0/T$ in excellent quantitative agreement with theory has been observed [27]. On the other hand, in UPt$_3$ [23] the observed $\kappa_0/T$ is significantly smaller than expected (and, in fact, barely resolvable) even though there is overwhelming evidence for nodes.

A possible test of the symmetry of the order parameter and the nature of potential nodes (imposed by symmetry vs accidental) is to investigate the effect of adding impurities. While impurity scattering will reduce the anisotropy of an $s$-wave gap (either by removing nodes or by increasing $\Delta_{\text{min}}$), it will lead to more zero-energy quasiparticles in a gap with $d$-wave symmetry, for example [28]. Both Nohara et al. [10] and Yokoya et al. [14] have interpreted their data on pure and impure YNi$_2$B$_2$C (specific heat and photoemission spectroscopy, respectively) in terms of an anisotropic $s$-wave gap.

On the question of a phonon mechanism, various authors [9] have argued that a standard Eliashberg analysis of $H_{c2}(T)$ and other data lead to a quantitatively satisfactory and consistent description of LuNi$_2$B$_2$C in terms of the measured phonon spectrum and a largely isotropic gap function. It remains to be seen whether such an analysis survives the inclusion of a very anisotropic gap.

In conclusion, we have shown the presence of highly delocalized quasiparticles throughout the vortex state of LuNi$_2$B$_2$C. The quasiparticle transport grows as a function of magnetic field in the same way as it does in UPt$_3$, an unconventional superconductor known to have a line of nodes in the gap, and not at all like $s$-wave superconductors. We conclude that the gap function of LuNi$_2$B$_2$C must have nodes in the gap, or at least deep minima. More work is necessary to determine precisely the location of these nodes or minima. Such pronounced gap anisotropy is unprecedented in phonon-mediated superconductivity, raising the question of whether phonons are indeed responsible for Cooper pairing in borocarbide superconductors, as has traditionally been thought.

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