Ultrasound Attenuation in Sr_2RuO_4: An Angle-Resolved Study of the Superconducting Gap Function

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(Received 19 January 2001)

We present a study of the electronic ultrasound attenuation α in the unconventional superconductor Sr_2RuO_4. The power law behavior of α at temperatures down to $T_c/30$ clearly indicates the presence of nodes in the gap. In the normal state, we find an enormous anisotropy of α in the basal plane of the tetragonal structure. In the superconducting state, the temperature dependence of α also exhibits significant anisotropy. We discuss these results in relation to possible gap functions.

DOI: 10.1103/PhysRevLett.86.5986 PACS numbers: 74.25.Ld, 74.20.Rp, 74.70.Pq

The symmetry of the order parameter Δ is of fundamental importance in understanding the nature of superconductivity. To this day, only two symmetries have been unambiguously identified among all known superconductors: s-wave symmetry in conventional superconductors and d-wave symmetry in some of the high-T_c cuprates. Both cases involve spin-singlet Cooper pairing. Heavy-fermion and organic superconductors are widely believed to be unconventional (i.e., not s-wave); however, for a variety of technical reasons, the symmetry of Δ has not been firmly established in any of these systems. In this context, Sr_2RuO_4 has emerged as a highly promising candidate for the study of unconventional superconductivity [1] because of its thoroughly characterized Fermi surface (FS) [2] and the availability of sizable high-quality crystals. Moreover, it may well prove to be the first clear example of a spin-triplet superconductor [3].

The most direct evidence for spin-triplet pairing is the absence of detectable change in the Pauli susceptibility below T_c as measured by ^{17}O Knight shift [4] and neutron scattering [5]. In addition, the appearance of a small random spontaneous internal field in the superconducting state [6] indicates that Δ breaks time-reversal symmetry, a conclusion supported by analysis of the square flux lattice [7]. The simplest Δ consistent with these two properties possesses an orbital wave function $\mathbf{d} = \hat{\mathbf{z}}(k_x + ik_y)$. This p-wave state has an isotropic gap (without nodes), and for several years it was viewed as the leading candidate for the superconducting order parameter of Sr_2RuO_4 [8].

However, in the last year it has become clear that an isotropic gap is inconsistent with the power law T dependence of several quantities observed deep in the superconducting state [9–12]. Such behavior is most naturally explained by line nodes in the gap. Thus the detailed symmetry of the order parameter in Sr_2RuO_4 is still very much an open question. In order to determine the *orbital* symmetry of Δ, one requires an angle-resolved probe to reveal the location of nodes in the gap on the FS. One approach is to seek an anisotropic response to an applied magnetic field. Such an effect has been observed in heat transport with the field rotating in the basal plane. However, the anisotropy was quite small and was deemed incompatible with vertical line nodes [10]. In the study presented in this Letter, we use the intrinsic angular resolution of ultrasound attenuation to directly probe the anisotropy of the quasiparticle excitation spectrum of superconducting Sr_2RuO_4 in zero magnetic field.

Moreno and Coleman have emphasized the power of ultrasound attenuation in studies of anisotropic superconductors [13]. In their model calculations, performed in the hydrodynamic limit where the electron mean free path l is much shorter than the sound wavelength λ, the low T power law behavior of $\alpha(T)$ is shown to depend strongly on the direction of sound propagation $\hat{\mathbf{q}}$ and polarization $\hat{\mathbf{e}}$ relative to the nodes. For example, in the case of a 2D gap with $k_x^2 - k_y^2$ symmetry and for transverse sound with $\hat{\mathbf{q}}$ and $\hat{\mathbf{e}}$ in the basal plane, quasiparticles at nodes along the $\langle 110\rangle$ are "inactive" when $\hat{\mathbf{q}} \parallel \langle 110\rangle$, yielding a strong $T^{3.5}$ power law, whereas they are maximally "active" in attenuating sound for $\hat{\mathbf{q}} \parallel \langle 100\rangle$, resulting in a weak $T^{1.5}$ dependence. In this way ultrasound attenuation experiments can locate nodes in the gap, as was done for the heavy-fermion superconductor UPt_3 [14].

We have performed measurements of longitudinal and transverse ultrasound attenuation in Sr_2RuO_4 in the temperature range 0.04–4 K, with sound propagating along the $\langle 100\rangle$ and $\langle 110\rangle$ directions in the basal plane of the tetragonal crystal structure. Our experiments were carried out on oriented pieces cut from a single high-quality crystal grown by the traveling solvent float zone technique [15]. T_c defined as the peak of the magnetic susceptibility (χ'') is 1.37 K. Samples were polished to 1 μm roughness, with two opposite faces whose parallelism was estimated to be better than 1.5 μm/mm. The alignment of the polished faces relative to the crystal axes was determined by Laue back reflection to be less than 0.5° off axis. (For

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propagation along $\langle 100 \rangle$, we estimate the misalignment to be 0.2–0.3°.) The crystals were 3.98 and 4.23 mm long, and had overlapping regions of the two parallel faces of $\sim 2\ \text{mm}^2$. Pulse-echo ultrasound was performed using a homebuilt spectrometer and commercial (30 MHz) $LiNbO_3$ transducers, bonded to the crystals with a thin layer of grease. With this technique, the absolute sound velocities can be measured to a few percent, but only a relative measurement of the electronic attenuation is possible because one cannot distinguish power losses from other origins. We denote the modes as follows: T100, T110, L100, and L110, where the polarization (T for transverse, L for longitudinal) is always in the plane. The indices denote the propagation direction. From the echo spacing, the sound velocities were found to be 3.30, 2.94, 6.28, and 6.41 $\text{mm}/\mu\text{s}$, respectively, within 3%. (These are somewhat different from previous reports [16].) Typically at low temperature for both the T100 and L110 modes we recorded more than 50 echoes, while L100 had at least 20 and T110 at least 2. Preliminary measurements were accomplished in a ^{3}He cryostat and were consistent with data taken in a dilution refrigerator up to 4 K. The results were also independent of excitation power.

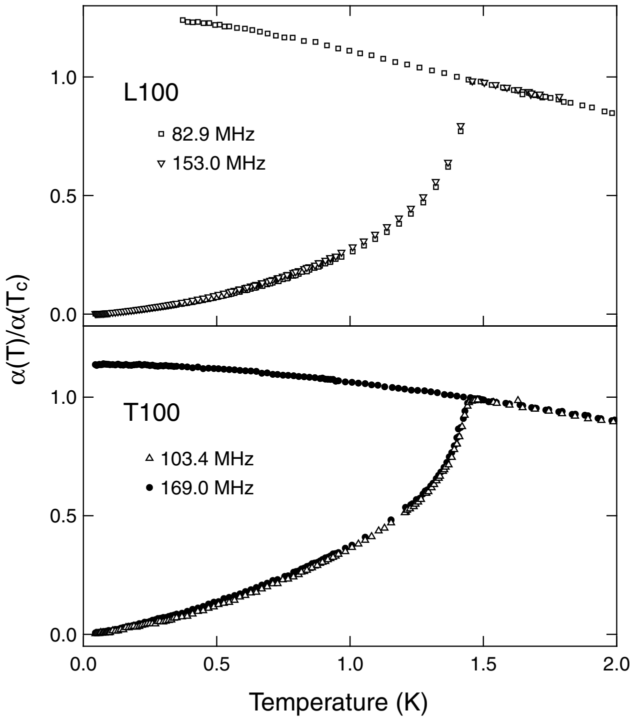

FIG. 1. Ultrasound attenuation $\alpha(T)$ normalized at T_c, both in the superconducting state ($B = 0$) and in the normal state ($B = 1.5\ \text{T} \perp c$). We show both T100 and L100 at different frequencies to demonstrate that the shape of the curves does not depend on frequency.

An important parameter that controls the behavior of the attenuation is the ratio λ/l. Theoretical approaches are quite different depending on the value of this parameter. The electronic mean free path below T_c is on the order of 1 μm, as estimated from either T_c or resistivity [17]. From this we expect that the crossover region $ql \sim 1$ (where $q = 2\pi/\lambda$ is the sound wave vector) from the hydrodynamic to the quantum regime occurs at 0.5 (1.0) GHz for the transverse (longitudinal) modes. The theoretical dependence of α on frequency is ν^2 in the hydrodynamic regime and ν in the quantum regime. Figure 1 shows data for two modes at two frequencies, normalized at T_c. The values of $\alpha(T_c)$ obey approximate ν^2 scaling, and the shape of $\alpha(T)$ is independent of ν and reproducible at many frequencies up to 500 MHz. We conclude that all our data are in the hydrodynamic limit.

In this limit, the attenuation is related to the 4th rank electronic viscosity tensor (η) via the relation [18]:

$$\alpha = \frac{(2\pi\nu)^2}{\rho c_s^3}\,\eta_{ijkl}\hat{e}_i\hat{q}_j\hat{e}_k\hat{q}_l = \frac{(2\pi\nu)^2}{\rho c_s^3}\,\bar{\eta}_{\text{mode}}\,, \quad (1)$$

where ρ is the mass density and c_s is the sound velocity for the mode with polarization and propagation directions $\hat{\mathbf{e}}$ and $\hat{\mathbf{q}}$. This defines $\bar{\eta}_{\text{mode}}$ as the linear combination of η_{ijkl} components for a particular mode. Under tetragonal symmetry there are 6 independent components of η, but only three determine the attenuation of the four in-plane modes, so that $\bar{\eta}_{\text{mode}}$ is given by η_{1212}, η_{1111}, $\frac{1}{2}(\eta_{1111} - \eta_{1122})$, and $\frac{1}{2}(\eta_{1111} + \eta_{1122} + 2\eta_{1212})$ for T100, L100, T110, and L110, respectively. We present $\bar{\eta}_{\text{mode}}$ in Fig. 2. The curves show that L100 and T110 have the same shape and almost the same amplitude. The L110 mode has a similar shape but a smaller amplitude. However, the T dependence of the T100 mode is clearly weaker and the magnitude of $\bar{\eta}_{\text{T100}}$ is *about 1000 times smaller* than $\bar{\eta}_{\text{L100}}$ or $\bar{\eta}_{\text{T110}}$. We note that the alignment of the crystal faces mentioned above is sufficient to yield the intrinsic $\bar{\eta}_{\text{T100}}$ [19]. Such a dramatic anisotropy of the normal state electronic η is unprecedented. Next we consider possible origins for this anisotropy.

The viscosity is related to the deformation of the FS caused by the sound wave's strain field, weighted by the electronic relaxation time τ [20]. The anisotropy of η may in part come from angular dependence of τ or the topology of the FS which is composed of three separate sheets (labeled α, β, and γ) [2]. Although the γ sheet is fairly isotropic, the α and β sheets have flat regions that could make significantly different contributions to the different components of η. Interband effects at the point of near contact between the three sheets may also be important. However, the anisotropy is so large that it probably requires significant variation in the electron-acoustic phonon coupling for the different modes, possibly originating in the highly directional nature of the Ru $4d$/O $2p$ hybrid orbitals that compose the conduction bands.

To facilitate discussion of $\alpha(T)$ below T_c, we continue with some remarks about the observed viscosities. The theory of 2D electronic viscosity [21] suggests a close relation between two of the relevant components, namely $\eta_{1111} = -\eta_{1122}$ for certain simple FS. The data presented

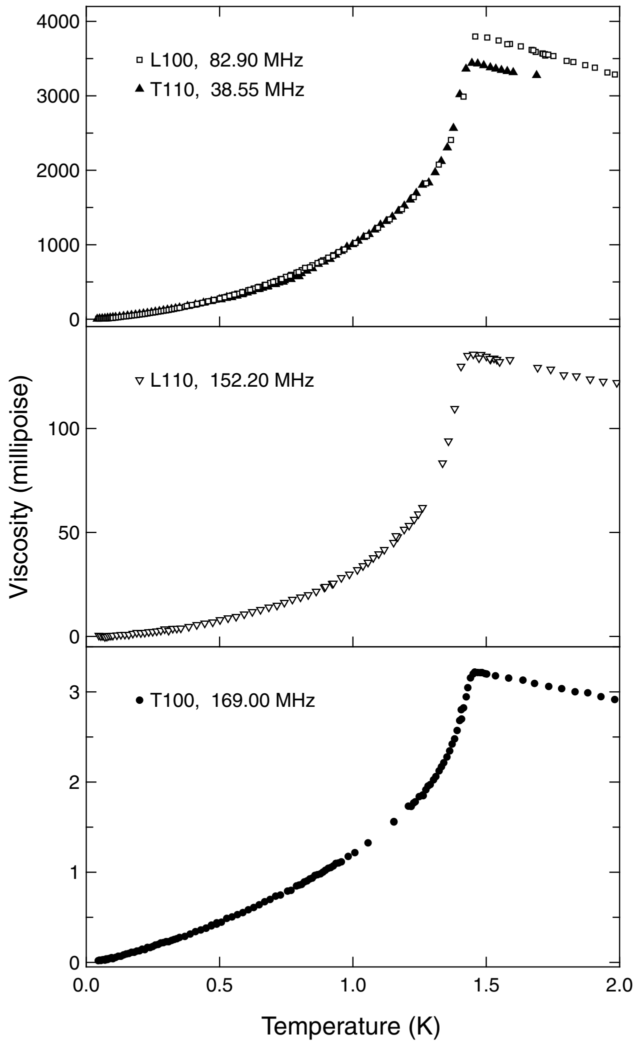

FIG. 2. Viscosity for the four in-plane modes. The viscosity η is related to the attenuation by $\eta = \alpha \rho c_s^3/(2\pi\nu)^2$, using a density $\rho = 5.9$ g/cm^3 and the sound velocities (c_s) given in the text (1 poise $\equiv$ 1 g/cm s). The data are extrapolated to 0 K to obtain the zero of the vertical axis.

in the top panel of Fig. 2 show that this relation is nearly fulfilled in Sr_2RuO_4, in both magnitude *and* T dependence. The slight imperfection of this symmetry should not be disturbing, since, e.g., the real FS is not exactly 2D. This relation also implies that $\bar{\eta}_{\mathrm{mode}}$ in the bottom two panels should be nearly equal. The apparent dramatic violation of this prediction is, however, a trivial consequence of the slight imperfection of the symmetry together with the enormous anisotropy ($|\eta_{1212}| \ll |\eta_{1111}|, |\eta_{1122}|$). While $\bar{\eta}_{\mathrm{L110}}$ contains all three viscosities, it is dominated by the slight inequality between $\bar{\eta}_{\mathrm{L100}}$ and $\bar{\eta}_{\mathrm{T110}}$ (as the difference is still much larger than η_{1212}). Because the observed $\bar{\eta}_{\mathrm{L110}}(T)$ is so similar to $\bar{\eta}_{\mathrm{L100}}(T)$, this difference is primarily one of magnitude. Thus there are effectively only two T dependences for the in-plane viscosities, one represented exclusively by $\bar{\eta}_{\mathrm{T100}}$ and the other most clearly by $\bar{\eta}_{\mathrm{L100}}$. We compare these in detail next.

The attenuation for these two modes is shown in Fig. 3, normalized by their normal state curves $\alpha_N(T)$ measured in a magnetic field (1.5 T, approximately in-plane) exceeding the upper critical field. A simple BCS model (weak-coupling isotropic s-wave gap) or a clean fully gapped p-wave state [22] gives an exponential decrease of $\alpha(T)$ at low T, such that below $\sim T_c/4$ the attenuation is essentially zero (solid line in Fig. 3). This is obviously not the case here, where we see power laws persisting down to $T_c/30$, *providing compelling evidence for the presence of nodes in the gap.* It is also clear that there is anisotropy in the T dependence of the viscosity in the basal plane. The weakest T dependence occurs for the T100 mode. Below 0.7 K, the normalized $\bar{\eta}_{\mathrm{T100}}$ and $\bar{\eta}_{\mathrm{L100}}$ are well described by the power laws $0.53t^{1.4}$ and $0.38t^{1.8}$, respectively, where $t = T/T_c$. The latter power law is consistent with another recent measurement of $\bar{\eta}_{\mathrm{T110}}$ [23]. The anisotropy revealed in Fig. 3 is much larger than any other kind of anisotropy observed so far in the basal plane of superconducting Sr_2RuO_4. Next we discuss the anisotropy of $\alpha(T)$ in relation to the nodal structure of the gap.

At the outset we note that the huge anisotropy in the normal state viscosity is not included in theories forming the basis of existing calculations of $\alpha(T)$ in the superconducting state. Thus, we can draw only tentative conclusions from a comparison of these theories to the data. We identify two types of order parameter that have been proposed: those with vertical line nodes (e.g., [21]) and those with horizontal line nodes (e.g., [24]). We now consider these in turn.

If the angular sensitivity articulated by Moreno and Coleman survives in a theory correctly accounting for the normal state viscosity, then the anisotropy of Fig. 3 is naturally interpreted in terms of vertical nodal lines. In this

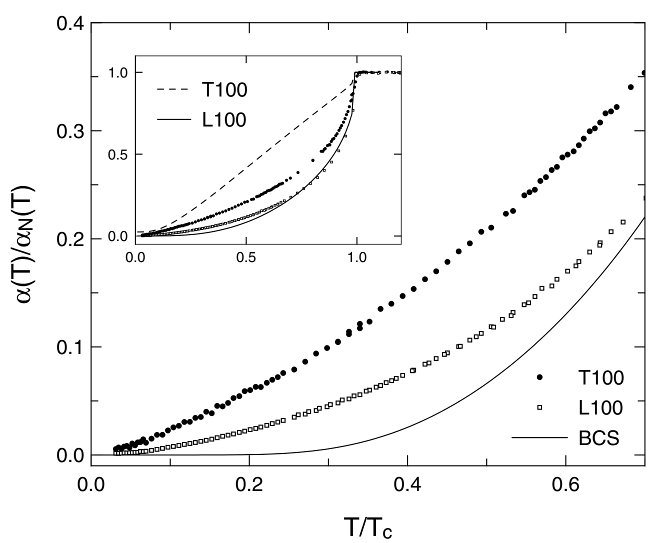

FIG. 3. $\alpha(T)$ divided by the normal state attenuation vs reduced temperature. The solid line is the simple BCS prediction. Inset: data up to T_c, compared with calculations for f-wave discussed in the text [21].

case, the observed anisotropy of the T dependence between L100 and T100 is qualitatively consistent with a Δ of $k_x^2 - k_y^2$ orbital symmetry in 2D such as found in the cuprates. However, given that a d-wave order parameter is inconsistent with the combination of spin-triplet symmetry and time-reversal symmetry breaking observed in Sr_2RuO_4, one needs to invoke *accidental* nodes, such as those of an f-wave state with $\mathbf{d} = \hat{\mathbf{z}}(k_x + ik_y)(k_x^2 - k_y^2)$ [24]. In the inset of Fig. 3, we compare our normalized data for L100 and T100 with the calculation of Graf and Balatsky [21] for such an f-wave gap on a single isotropic 2D FS [25]. In detail the T dependences differ significantly from the simple model predictions. There is good overall agreement for the L100 mode; however, the low T power law exponent is much lower than expected (1.8 vs 3.5). The data for the T100 mode is always below the calculated curve, but, in contrast, the exponent is close to the predicted 1.5 [13,21]. These significant differences may be the consequence of the real FS of Sr_2RuO_4 or of a more complex nodal structure. Detailed calculations are needed to evaluate how strongly the observed anisotropic T dependence favors such a Δ.

For a simple horizontal line node, one would not expect anisotropy in the plane. Thus we must presume a separate source of the observed anisotropy. One possibility is a (non-nodal) fourfold variation of $|\Delta|$ in the plane. The magnitude of the modulation required to explain our data could be computed and the resulting gap function compared with other measurements such as the electronic specific heat. However, at sufficiently low T, we still expect the power law exponent to be isotropic in this scenario.

In summary, the power law T dependence of the ultrasound attenuation persisting down to $T_c/30$ establishes unambiguously the existence of nodes in the gap function of Sr_2RuO_4. These power laws and the anisotropy of the attenuation in the superconducting state exclude the possibility of a pure nodeless p-wave state, but may prove to be consistent with a state that has either vertical nodes on the diagonal or a horizontal line of nodes in conjunction with significant fourfold gap modulation. A detailed calculation taking into account the real (multisheet) FS of Sr_2RuO_4 and the large normal state anisotropy is needed to properly extract the full order-parameter information contained in the anisotropy and temperature dependence of $\alpha(T)$.

We would like to thank M. J. Graf for useful discussions and R. W. Hill for his help with the experiments. This work was supported by the Canadian Institute for Advanced Research and funded by NSERC. C. L. acknowledges the support of the Walter C. Sumner Foundation and of FCAR (Québec).

Note added in proof.—We find that a two component model which is the sum of a power law and a BCS temperature dependence provides a good description of $\alpha(T)$ all the way to T_c. This may lend support to theories, such as that of Zhitomirsky and Rice [26], which find that a nodeless order parameter on one sheet of the FS induces a nodal one on the other sheets. Detailed analysis along these lines will be published elsewhere. Note also that Walker *et al.* [27] have recently calculated the electron-phonon coupling for Sr_2RuO_4 and are able to account for the large anisotropy of the normal state attenuation.

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