Investigation of the Superconducting Gap in $La_{2-x}Sr_xCuO_4$ by Raman Spectroscopy

X. K. Chen and J. C. Irwin
Department of Physics, Simon Fraser University, Burnaby, British Columbia, V5A 1S6 Canada

H. J. Trodahl*
Department of Physics, University of British Columbia, Vancouver, British Columbia, V5A 1S6 Canada

T. Kimura and K. Kishio
Department of Applied Chemistry, University of Tokyo, Tokyo 113, Japan
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The low energy Raman spectra of a $La_{1.83}Sr_{.17}CuO_4$ single crystal have been measured at temperatures above and below T_c. The redistribution of the electronic continua that occurs as a result of the opening of the superconducting gap has been observed. Based on the polarization dependence of the continua, it is concluded that the superconducting gap $\Delta(\mathbf{k})$ is anisotropic, with nodes along the $(\pm 1, \pm 1)$ directions and maxima along the $(0, \pm 1)$ and $(\pm 1, 0)$ directions. The maximum pairing energy $2|\Delta_{\max}|$ is estimated to be about $7.7kT_c$.

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The symmetry of the pairing state is believed to be an important key in arriving at an understanding of the mechanism of superconductivity in the high-temperature superconductors. For example, it has been shown [1,2] that pairing in a state with $d_{x^2-y^2}$ symmetry results when the pairing is induced by the exchange of antiferromagnetic spin fluctuations. A number of experiments [3–10] have been interpreted as providing support for the existence of an anisotropic nodal (s- or d-wave) gap in $YBa_2Cu_3O_y$ (Y123) and $Bi_2Sr_2CaCu_2O_8$ (Bi2212). On the other hand, in the only study of the gap anisotropy in $La_{2-x}Sr_xCuO_4$ [La214(x)] that we are aware of, Mason *et al.* [11] obtained results that are most easily understood in terms of an isotropic order parameter. They carried out neutron scattering and specific heat measurements on La214(0.14) and found low energy ($<3.5k_BT_c$) excitations at temperatures well below T_c, which ruled out the possibility of a clean s-wave gap. No anisotropic features characteristic of a simple d-wave gap were found, and they concluded that their data were consistent with La214 being a gapless s-wave superconductor. Given that there are relatively few experimental results pertaining to the gap symmetry in La214, and furthermore that these results lead to a picture of the gap which is at variance with that suggested by experiments [3–10] on Bi2212 and Y123, further investigations of the gap in La214 are clearly suggested. In particular, we would like to directly compare the electronic excitations across the superconducting gap on different regions of the Fermi surface. This type of information can be obtained [12] from inelastic light scattering experiments, and in this Letter we present the results of the first Raman scattering study of the superconducting order parameter in La214.

A typical feature [12,13] in the Raman spectra of superconductors is a low energy continuum that arises from scattering from electronic excitations on the Fermi surface. As the temperature is decreased below T_c, the frequency distribution of the electronic continua changes [12,13] to reflect the opening of the superconducting gap. Analysis of the electronic continua above and below T_c can provide important information about the superconducting gap $\Delta(\mathbf{k})$. In certain cases, by appropriately choosing the polarizations of the incident and scattered light, one can selectively probe [12] different regions of the Fermi surface, and hence obtain information about the $\mathbf{k}$ dependence of the gap. A theoretical description of electronic Raman scattering from superconductors with a short coherence length was first developed by Klein and Dierker [13]. Recently their approach has been used [8,9] in an attempt to describe results obtained from the high-T_c cuprates, and this formalism will be used to discuss the spectra presented in this paper.

The high-quality La214(0.17) (T_c = 37 K) single crystal used in this study was grown by a traveling solvent floating-zone method, as previously described [14]. Specimens with dimensions which were typically $2 \times 2 \times 0.5$ mm^3 were cut from a single crystal and oriented using Laue x-ray diffraction patterns. The surfaces of the sample were polished with diamond paste and etched with a bromine-ethanol solution [15]. The Raman spectra were obtained in a quasibackscattering geometry using the 514.5 nm line of an Ar-ion laser, which was focussed onto the sample with a cylindrical lens to provide an excitation level of about 10 W/cm^2. By examining the laser power dependence of the Raman spectra and the intensity ratio between the Stokes and anti-Stokes spectra, the temperature of the excited region of the sample was found to be about 11 K

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above ambient. The temperatures reported in this paper will be the actual temperatures in the excited region of the sample.

The Raman spectra measured in the $z(xx)\bar{z}$, $z(x'x')\bar{z}$, $z(xy)\bar{z}$, and $z(x'y')\bar{z}$ geometries are shown in Fig. 1. Here x and y are parallel to the Cu-O bonds and x' denotes the $(1,1,0)$ polarization and y' the $(-1,1,0)$ polarization. Considered within the tetragonal point group D_{4h}, the $x'y'$ geometry allows coupling to excitations with B_{1g} symmetry, the xy geometry to the B_{2g} component, and the xx ($x'x'$) geometry to a combination of the A_{1g} and B_{1g} (B_{2g}) components [6,8]. In the remainder of this paper we will primarily be concerned with the Raman continua taken in the $x'y'$ and xy geometries which allows us to isolate the B_{1g} and B_{2g} components of the electronic excitations on the Fermi surface.

As shown in Fig. 1, when the temperature is decreased below T_c, a typical superconductivity-induced redistribution of the electronic continua is observed in all the scattering geometries investigated. In particular, a broad maximum appears at about 200 cm^{-1} in the $x'y'(B_{1g})$ geometry and at about 130 cm^{-1} in the $xy(B_{2g})$ geometry. In the $x'x'$ (and xx) geometry, the maximum of the continuum is masked by the 145 cm^{-1} A_{1g} phonon but might appear as a shoulder near 125 cm^{-1}. Thus all of the continua (Fig. 1) are depleted at low frequencies and exhibit a broad maximum whose frequency depends on the scattering geometry. It is interesting to note that in this respect the La214 spectra shown in Fig. 1 are qualitatively similar to results obtained from other high-T_c cuprates. To make this comparison more quantitative one can also note that the frequencies of the continua maxima in La214, Y123 [6,16], and Bi2212 [7,8] appear to scale with the critical temperature such that the A_{1g} and B_{1g} maxima occur at about $5k_BT_c$ and $8k_BT_c$, respectively, in all three compounds. These observations would appear to provide support for the connection that has been made [6–8] between the redistribution of the continua that occurs below T_c and the opening of the superconducting gap in the high-T_c cuprates and further suggest that the sensitivity [7,16] of the B_{1g} continuum of Y123 to doping should be attributed to Fermi surface effects [17,18] and not to scattering from alternate sources such as spin fluctuations.

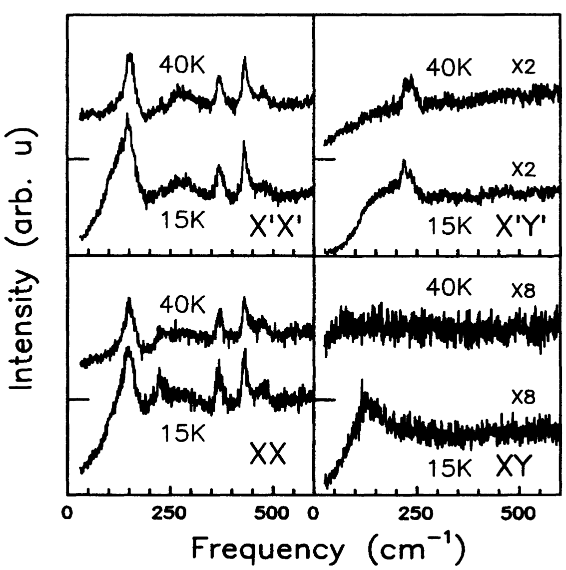

FIG. 1. Raman spectra of $La_{1.83}Sr_{0.17}CuO_4$ obtained at 40 and 15 K in the $x'y'$ (B_{1g}), xy (B_{2g}), $x'x'$ ($A_{1g}+B_{1g}$), and xx ($A_{1g}+B_{1g}$) scattering geometries.

In conventional superconductors with an isotropic gap, one does not expect to observe any scattering for frequencies $\omega \le 2\Delta$. However, as shown in Fig. 1, the low frequency depletion in La214 is not complete. In other words, there is residual scattering from electronic excitations at energies well below the BCS figure for the gap energy ($2\Delta = 3.5kT_c = 88$ cm^{-1}). This is consistent with the recent neutron scattering results and specific heat measurements in $La_{2-x}Sr_xCuO_4$ ($x = 0.14$) [11]. It should be noted that the residual scattering in the $x'y'$ (B_{1g}) geometry is considerably weaker than that measured in other geometries. The scattering-geometry dependence of both the residual scattering and the peak frequency of the continuum is in fact a consequence of the anisotropy of the superconducting gap function $\Delta(\mathbf{k})$, as will be explained in the following discussion.

In the high-T_c cuprates, the penetration depth λ is much greater than the coherence length ξ. The relevant wave vector transfer q in a metal is about λ^{-1}, and hence the cuprates are treated in the small wave vector ($q \to 0$) limit [13]. In this limit the photon cross section for Raman scattering from pairs of superconducting quasiparticles is given by [13]

$$\frac{d^2R}{d\omega d\Omega} = \frac{4N(0)r_0^2}{\omega}\left\langle \frac{|\gamma_k|^2|\Delta(\mathbf{k})|^2}{(\omega^2 - 4|\Delta(\mathbf{k})|^2)^{1/2}} \right\rangle, \quad (1)$$

where $N(0)$ is the density of states for one spin, r_0 is the Thomson radius, $\gamma(\mathbf{k})$ is the Raman vertex, and $\langle\cdots\rangle$ denotes an average [13] over the Fermi surface with the restriction that $\omega^2 > 4\Delta^2(\mathbf{k})$. In the nonresonant limit, the components of $\gamma(\mathbf{k})$ are given by [19]

$$\gamma_{ij}(\mathbf{k}) = \frac{m}{\hbar^2}\mathbf{e}^I \cdot \frac{1}{m^*} \cdot \mathbf{e}^S = \frac{m}{\hbar^2} e_i^I \frac{\partial^2 \varepsilon(\mathbf{k})}{\partial k_i \partial k_j} e_j^S . \quad (2)$$

Here m^* is the generalized effective mass tensor, $\mathbf{e}^I$ and $\mathbf{e}^S$ denote the polarization vectors of the incident and scattered light, and $\varepsilon(\mathbf{k})$ is the dispersion relation of the conduction band. From Eq. (2) it is evident that one can choose a different scattering geometry to achieve a different $\mathbf{k}$ dependence in $\gamma(\mathbf{k})$ and thus probe the superconducting gap on different parts of the Fermi surface (FS). For example, for a given band structure $\varepsilon(\mathbf{k})$ and scattering geometry, if $\gamma(\mathbf{k})$ is constant on the FS or has the same $\mathbf{k}$ dependence as $\Delta(\mathbf{k})$, the continuum will be peaked at $2|\Delta_{\max}|$, where $|\Delta_{\max}|$ is the maximum gap energy on the FS. On the other hand, if $\gamma(\mathbf{k})$ vanishes near the gap maxima, the peak frequency of the continuum should be below $2|\Delta_{\max}|$. It is thus clear that the anisotropy of the superconducting gap can be probed by exploiting the symmetry properties of the different components of $\gamma(\mathbf{k})$. For example, the B_{1g} component of the Raman vertex $\gamma_{B_{1g}}(\mathbf{k})$ transforms in the same way as the function $k_x^2 - k_y^2$. Consequently, in the two-dimensional k space associated with the CuO_2 planes, $\gamma_{B_{1g}}(\mathbf{k})$ should vanish along $(\pm 1, \pm 1)$ and have maxima in the directions $(0, \pm 1)$ and $(\pm 1, 0)$. On the other hand, $\gamma_{B_{2g}}(\mathbf{k})$ transforms as $k_x k_y$ and thus vanishes along $(0, \pm 1)$ and $(\pm 1, 0)$ and has maxima along $(\pm 1, \pm 1)$. To illustrate, we have evaluated (see Fig. 2) the $k_{x'} k_{y'} (B_{1g})$ and $k_x k_y (B_{2g})$ components of the effective mass using a second nearest neighbor tight-binding model [9] to determine $\varepsilon(\mathbf{k})$ and the FS. The model parameters ($s/t = -0.3$, $\mu/2t = -0.58$, $t = 1$) were chosen to yield a FS (Fig. 2) similar to that used by previous workers [20–22]. The distinct difference in the angular dependence between $\gamma_{B_{1g}}$ and $\gamma_{B_{2g}}$ is ideal for studying the gap anisotropy, especially for testing the d-wave pairing model.

For the purpose of illustration we have also calculated the B_{1g} and B_{2g} Raman continua for both a d-wave [1,9] gap [Fig. 3(b)] and an isotropic s-wave [13] gap [Fig. 3(c)]. It must be noted that a definitive estimate of the spectra would require a much more detailed knowledge of the band structure than is provided by the tight-binding model. Given this reservation, however, it should be noted that the results shown in Figs. 2 and 3 are not particularly sensitive to the parameters used in the tight-binding model. Changing the FS, for example, alters the relative magnitudes of the B_{1g} and B_{2g} lobes in Fig. 2 and hence the relative magnitudes of the peaks in the continua, but the frequency difference between the peaks in the B_{1g} and B_{2g} continua is determined primarily by the anisotropy of $\Delta(\mathbf{k})$.

For comparison purposes, the measured B_{1g} and B_{2g} electronic continua are shown in Fig. 3(a). It is clear that the peak frequency of the B_{1g} continuum is higher than that found in the B_{2g} geometry, in agreement with the model predictions [Fig. 3(b)]. The depletion at low frequencies is also strongest in the B_{1g} geometry [Figs. 3(a) and 3(b)], and, as a result, at low energies (≤ 100 cm^{-1}), the B_{1g} slope is very small. Considering the angular dependence of $\gamma_{B_{1g}}$ and $\gamma_{B_{2g}}$ means that the superconducting gap energy $\Delta(\mathbf{k})$ has its maxima along $(0, \pm 1)$ and $(\pm 1, 0)$ and minima along $(\pm 1, \pm 1)$. If the central frequency of the peak in the B_{1g} continuum is taken to be a measure of the maximum gap energy, we obtain $2|\Delta_{\max}| \approx 200$ cm^{-1} $\approx 7.7\, k_B T_c$. As far as the minimum gap energy is concerned, since the intensity of the B_{2g} continuum does not appear to vanish even at frequencies below 30 cm^{-1}, $|\Delta|_{\min}$ must be less than 15 cm^{-1}. In fact, the intensity of the B_{2g} continuum extrapolates to zero at zero frequency, which suggests $|\Delta|_{\min} = 0$, and the density of states vanishes at the gap minima. This behavior, and the enhanced low frequency depletion of the B_{1g} spectrum, strongly suggests that the superconducting gap function $\Delta(\mathbf{k})$ has nodes along $(\pm 1, \pm 1)$. In other words, the differences between the B_{1g} and B_{2g} electronic continua clearly indicate that the superconducting gap in La214 is anisotropic, and the angular dependence of the gap energy $|\Delta(\mathbf{k})|$ is qualitatively the same as $|\gamma_{B_{1g}}|$, which is illustrated in Fig. 2(a). The gap anisotropy is thus consistent with $d_{x^2-y^2}$ symmetry [1], in that there are nodes along $(\pm 1, \pm 1)$ and maxima along the $(0, \pm 1)$ and $(\pm 1, 0)$ directions. However, it must be noted that the phase of the gap function $\Delta(\mathbf{k})$ plays no role in Eq. (1), since only $|\Delta^2(\mathbf{k})|$ appears in the equation. Therefore, an analysis based on Eq. (1) cannot distinguish the difference

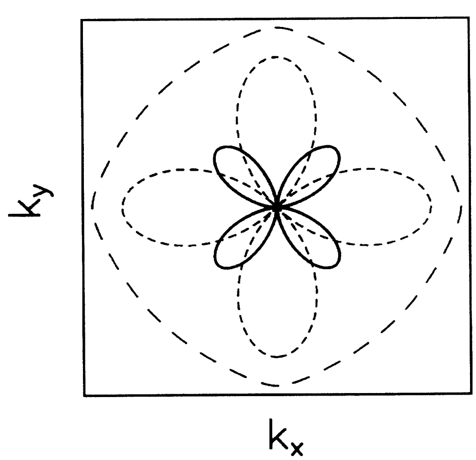

FIG. 2. A plot of the absolute value of $x'y'$ (B_{1g}) component (short-dashed lines) and the xy (B_{2g}) component (solid lines) of the reciprocal effective mass tensor (2) evaluated on the Fermi surface, depicted by the long dashed line (centered at π, π).

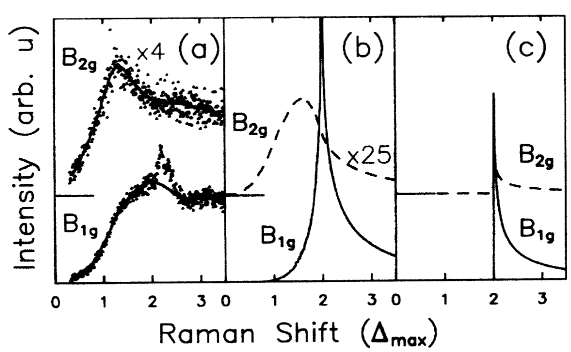

FIG. 3. (a) A comparison of the B_{1g} and B_{2g} Raman continua obtained at 20 K. The solid lines represent a spline fit to the electronic continua. (b) The calculated continua using (1) and (2) for a d-wave gap, $\Delta(\mathbf{k}) = \Delta_0(\cos k_x a - \cos k_y a)$. (c) The calculated continua for an isotropic s-wave gap.

between a d-wave $k_x^2 - k_y^2$ and an anisotropic s-wave $|k_x^2 - k_y^2|$ gap.

In summary, we have carried out measurements of the low energy Raman continua of $La_{1.83}Sr_{0.17}CuO_4$ in the $xx, x'x', xy$, and $x'y'$ scattering geometries and have carried out the first Raman study of the superconducting gap in La214. As the sample is cooled below T_c, a broad peak whose central frequency depends on the polarization appears in each of the continua. This behavior is similar to that observed in Y123 [6,16] and Bi2212 [7,8], and a comparison of spectra obtained from these compounds reveals that the peaks in the spectra scale with T_c as would be expected if the scattering resulted from the excitation of quasiparticles across a superconducting gap. Based upon the observed polarization dependence of the spectra and the symmetry properties of the Raman vertex, it is concluded that the superconducting gap in La214 is anisotropic with nodes along $(\pm 1, \pm 1)$ and maxima along the x and y axis.

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*Permanent address: Department of Physics, Victoria University of Wellington, P.O. Box 600 Wellington, New Zealand.

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