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Phonon Raman scattering in superconducting $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$

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We have performed Raman scattering experiments on the high-$T_c$ superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$ ($T_c = 37$ K). We observe three of the four Raman-active optical-phonon modes and, on the basis of a comparison to the Raman spectra of $K_2\text{MnF}_4$, are able to tentatively assign the mode symmetries. No anomalous temperature dependence is observed for all three modes, indicative of the lack of strong electron-phonon coupling in these modes.

Recently superconductivity in the system $(\text{La},X)_2\text{CuO}_4 - \gamma$ ($X = \text{Ba},\text{Sr}$) has been found\(^1\) with transition temperatures $T_c$ up to $\approx 40$ K, which is almost 100% higher than the previously highest $T_c$ of about 23 K in $\text{Nb}_2\text{Ge}_3$.\(^5\) In the conventional BCS theory of superconductivity, a high $T_c$ results from strong electron-phonon coupling. Strong electron-phonon coupling is anticipated for $(\text{La},\text{Sr})_2\text{CuO}_4$ due to the nearly ideal nesting conditions of the Fermi surface that arise from the planar structure of this compound.\(^6\) Indeed, a Peierls transition in undoped $\text{La}_2\text{CuO}_4 - \gamma$ from tetragonal to orthorhombic crystal structure is found\(^7\) at $260\ ^\circ$C. However, there also has been the suggestion\(^7\) that Cooper pairing in this new class of high-$T_c$ materials does not arise from phonon coupling but is primarily due to electronic coupling produced by resonating $\text{Cu} - \text{O}$ valence bonds. This is appealing because, as McMillan\(^8\) pointed out, soft phonons, which are responsible in part for enhanced electron-phonon coupling, also lead to lattice instabilities and can place an upper limit on $T_c$. Subsequent work by Allen and coworkers\(^9\) showed that McMillan's constraints were unnecessarily severe, but that there may still be a limiting value for $T_c$. In any case, microscopic information on the lattice dynamics of $(\text{La},\text{Sr})_2\text{CuO}_4 - \gamma$ is highly desirable to arrive at a microscopic understanding of superconductivity in this new class of high-$T_c$ superconductors.

We have performed Raman scattering experiments on $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$ in an attempt to reveal the basic mechanism for Cooper pairing in this compound. Our sample was made by grinding the oxides and firing the pressed mixture three times at $1100 \ ^\circ$C in an oxygen atmosphere. The resulting powder was pressed into a pellet. The superconducting transition temperature was determined to be 37 K from dc magnetic-susceptibility measurements\(^12\) which also showed diamagnetism of 55% of $1/4\pi$ at 2 K, when the sample was cooled in zero applied field below $T_c$. $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$ crystallizes in the tetragonal space group $D_{4h}^4$ ($I4/mmm$) having two formula units per unit cell. The different $q = 0$ phonon modes of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$ are listed in Table I, with the four Raman-active (RA) modes displayed\(^13\) in Fig. 1. One $A_{1g}$ and one $E_g$ mode are due to oxygen vibrations and the other $A_{1g}$ and $E_g$ modes result from movements of the lanthanum ion.

In Fig. 2 we show Raman spectra of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 - \gamma$ as a function of temperature. Because our sample was polycrystalline, we could not perform a symmetry analysis of the observed peaks. However, from comparison with the symmetry analysis of the Raman spectrum of isostructural $K_2\text{MnF}_4$ (Ref. 14) or $K_2\text{CuF}_4$\(^15\) we can tentatively assign the peaks in Fig. 2 to the following symmetries: The lanthanum $A_{1g}$ mode is at 100 cm$^{-1}$ scaled down from the value of the potassium $A_{1g}$ mode in $K_2\text{MnF}_4$ (180 cm$^{-1}$) by the square root of

FIG. 1. Raman-active modes of $(\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_4 - \gamma$ with $D_{4h}^4$. Filled circles denote Cu atoms, large open circles O-atoms, and small open circles La atoms (Sr atoms), respectively.

<table>
<thead>
<tr>
<th>Type</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman active</td>
<td>$2 \times A_{1g}$, $2 \times E_g$</td>
</tr>
<tr>
<td>Infrared active</td>
<td>$3 \times A_{2u}$, $4 \times E_u$, $1 \times B_{2u}$</td>
</tr>
<tr>
<td>Translational</td>
<td>$1 \times A_{2u}$, $1 \times E_u$</td>
</tr>
<tr>
<td>(acoustic modes)</td>
<td>. . .</td>
</tr>
<tr>
<td>Others</td>
<td>. . .</td>
</tr>
</tbody>
</table>

TABLE I. Factor-group analysis of the $q = 0$ lattice vibrations of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ crystallizing in the $K_2\text{NiF}_4$ structure ($D_{4h}^4$ or $I4/mmm$).
FIG. 2. Raman spectra of \((\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_{4-y}\) for selected temperatures between 300 and 6 K. The oxygen \(A_{1g}\) mode is near 400 cm\(^{-1}\), the oxygen \(E_g\) mode near 180 cm\(^{-1}\), and the lanthanum (strontium) \(A_{1g}\) mode near 100 cm\(^{-1}\).

The mass ratio of potassium and lanthanum. The lanthanum \(E_g\) mode consequently is expected at 50 cm\(^{-1}\) and is probably too weak in intensity to be observed, as we tried without success to find any mode in that energy region. The oxygen \(A_{1g}\) mode is at 380 cm\(^{-1}\) similar to the fluorine \(A_{1g}\) mode in \(\text{K}_2\text{MnF}_4\) and the oxygen \(E_g\) mode is near 180 cm\(^{-1}\) also in good agreement from what is expected from the reference compounds. The oxygen \(A_{1g}\) mode is, however, broader and weaker compared to the fluorine \(A_{1g}\) mode in \(\text{K}_2\text{MnF}_4\).

Variation of the temperature has little effect on the Raman spectra of \((\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_{4-y}\) as can be seen from Fig. 2. In Figs. 3 and 4 the linewidths and peak positions, respectively, are plotted as a function of temperature for the lanthanum \(A_{1g}\) mode and the oxygen \(A_{1g}\) mode. The signal of the oxygen \(E_g\) mode was too weak to yield reliable detailed information. The lanthanum \(A_{1g}\) mode does not have a significant temperature dependence in either its position or its linewidth. It is, however, surprising that we do not observe a splitting of this peak due to the presence of Sr, since its mass is quite different from that of La. In

FIG. 3. Peak position of the oxygen \(A_{1g}\) mode and the lanthanum \(A_{1g}\) mode as a function of temperature.

FIG. 4. Linewidth (full width at half maximum) of the oxygen \(A_{1g}\) mode and the lanthanum \(A_{1g}\) mode as a function of temperature.
any case, this is indicative of a very homogeneous mixing of the Sr into the lattice. For the oxygen $A_{1g}$ mode one observes an unusually large linewidth (46 cm$^{-1}$ at 300 K). This is probably related to oxygen deficiencies, which are anticipated for La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$, from the behavior of all perovskites. Deficiencies break the translational invariance of the system, thereby destroying $q$ conservation and allowing Raman scattering from $q\neq 0$ oxygen modes. Because these modes are not dispersionless, this results in line broadening. This can also cause a shift in peak position, and a spatially inhomogeneous distribution of oxygen deficiencies could, therefore, explain the scatter in the peak position of the oxygen $A_{1g}$ mode, as can be seen from Fig. 3. This is not observed for the lanthanum $A_{1g}$ mode. As a general trend of the data we observe, similar to the behavior of the lanthanum $A_{1g}$ mode, a broadening of the oxygen $A_{1g}$ mode and a nearly temperature-independent peak position.

To summarize our experimental results, the observed Raman-active phonons of La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$ do not reflect strong electron-phonon coupling effects, which should result in a softening and line broadening of these modes upon cooling the sample below $T_c$. The large linewidth of the oxygen $A_{1g}$ mode is quite unusual and seems to be related to oxygen deficiencies in our sample.

Our Raman scattering results can be put in the following way into the context of what is known or imagined about La$_{2-x}$Sr$_x$CuO$_4$-$\gamma$. Most simply one could say, if the Cooper pairing of the electrons is primarily electronic in nature, one should of course not observe any phonon anomalies. On the other hand, phonons modulating the Cu—O bond lengths in the $x$-$y$ plane, which are only infrared (IR) active, should exhibit the strongest electron-phonon coupling because they provide the nesting of the Fermi surface in pure La$_3$CuO$_4$-$\gamma$. Consequently, probably the most pronounced electron-phonon coupling cannot be probed by Raman scattering, and our results do not completely rule out strong electron-phonon coupling in La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$. Absence or presence of strong electron-phonon coupling in La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$ has to be proven conclusively by IR spectroscopy or neutron scattering. However, it is surprising that a strong electron-phonon coupling in the Cu-O planes, necessary to explain a $T_c$ of 37 K in conventional BCS terms, should have absolutely no effect on the lattice dynamics of those layers not containing Cu.

In conclusion, we have observed three of the four Raman-active modes of La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$, none of them exhibiting features indicative of strong electron-phonon coupling. Because Raman scattering is insensitive to phonons modulating the Cu—O bonds, our results do not permit a definitive statement concerning the pairing mechanism in La$_{1.85}$Sr$_{0.15}$CuO$_4$-$\gamma$.

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6F. Mueller (private communication).