RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 6 1 FEBRUARY 1993-II

Inelastic light scattering from electronic and phononic excitations in normal and superconducting $Tl_2Ba_2CuO_6$ single crystals

R. Nemetschek, O. V. Misochko,* B. Stadlober, and R. Hackl
Walther-Meissner-Institut für Tieftemperaturforschung, 8046 Garching, Federal Republic of Germany
(Received 4 November 1992)

We report results of Raman-scattering experiments on electronic and phononic excitations in single-crystalline $Tl_2Ba_2CuO_6$ with one Cu-O layer and a T_c of 80 K. The electronic scattering is similar to that in other Cu-O compounds, revealing a symmetry-dependent carrier relaxation rate above T_c and a characteristic redistribution of scattering intensity below T_c. The maximum pairing energy $2\Delta_0$ estimated from the spectra is between 8 and $9kT_c$. In addition to the Raman-allowed phonons several new lines and bands are found which we believe to originate from the reduced symmetry of the Tl-O layers. The intensities of all phonon lines depend sensitively on the excitation wavelength.

Tl-based Cu-O superconductors exhibit the highest transition temperatures observed so far. Since T_c is considerably larger than the boiling point of liquid nitrogen, these compounds are among the most promising ones for technological applications. Several peculiarities of the physical properties, too, demand attention and detailed studies. For instance, the maximum T_c does not strongly depend on the number of Cu-O layers per structural unit as in the Bi-based compounds and may be as high as 115 K in single-layer $Tl_2Ba_2CuO_6$(Tl 2:2:0:1).[1] Pronounced phonon anomalies have been found in this material class by ir spectroscopy[2] exceedingly those observed in other high-temperature superconductors (HTSC's). In Tl 2:2:0:1 T_c can be varied between approximately zero and 100 K simply by changing the oxygen content.[3] Thus, similar to the $(La_{1-x}Sr_x)_2CuO_4$ system, a large range of the phase diagram is accessible for experiments. Nevertheless, since single crystals cannot be obtained easily, the information for the monolayer compound available so far is limited. Recently, the spin dynamics of Tl 2:2:0:1 with various transition temperatures have been studied.[4] The energy gap could then be estimated, but only for samples with T_c close to the maximum. To our knowledge, neither optical nor tunneling experiments have been carried out for studying the order parameter in single crystals. Therefore, Raman experiments on Tl 2:2:0:1 may close a gap in the information, particularly as this technique has turned out to be useful in studying phononic as well as electronic excitations. The latter ones may reveal the carrier dynamics in the normal state[5] and the superconducting order parameter,[6] if they indeed originate from spontaneous inelastic light scattering.

In this paper, we present results of detailed Raman-scattering experiments on superconducting Tl 2:2:0:1 single crystals. Electronic and phononic excitations will be studied as a function of temperature and polarization. Energy loss and energy gain spectra will be compared. The paper focuses particularly on electronic excitations in the superconducting state in order to elucidate properties of the energy gap and its symmetry dependence. Finally, some peculiarities of the phonons will be discussed.

Single crystals of the 2:2:0:1 phase were obtained using a self-flux method.[1] The crystals had a tetragonal unit cell with point group $D_{4h}^{17}(I4/mmm)$. The superconducting transition temperatures of different crystals from one batch varied between zero and 115 K. The actual composition of the selected sample was determined by microprobe analysis to be $(Tl_{1.85}Cu_{0.12})Ba_{2.0}Ca_{0.032}CuO_6$. As indicated in the formula some of the thallium ions were replaced by copper. Here all atoms were found at the appropriate symmetry positions, while thallium and oxygen were shifted in the direction of the bonds by 0.11 and 0.28 Å respectively, with no copper present.[1] Unlike in Bi 2:2:1:2, however, no long-range order is established. The Ca contamination was close to the background level of approximately 3%. The magnetization was measured in fields of 0.4 and 4 Oe both parallel and perpendicular to the Cu-O planes. Approximately 80% of the volume, attributed to the 2:2:0:1 phase, became superconducting at an onset temperature of 80 K. Above this temperature no sign of superconductivity was found in the Raman spectra. The magnetization saturated between 60 and 70 K. Two additional transitions at 100 and 125 K are most likely an indication of the 2:2:1:2 and the 2:2:2:3 phase, respectively, though detected neither by x-ray nor by Raman analysis. Therefore, the volume fraction of the multilayer phases is estimated to be of the same order of magnitude as the Ca contamination and may be neglected in the following.

Details of the experimental setup are given elsewhere.[7] The spectral resolution of the monochromator was set at about 10 cm^{-1}. In order to obtain a mirrorlike surface the crystal was cut by an ultramicrotome. For excitation the Ar^+ laser lines at 514 and 458 nm were chosen. To minimize the heating of the illuminated spot the absorbed laser power did not exceed 4 mW. The actual sample temperature was estimated from the Stokes to the anti-Stokes ratio for each experiment. The polarizations of the incident and the scattered light were always in the a-b plane and will be represented in the Porto notation with $x=[100]$, $x'=[110]$, etc. In a tetragonal crystal the $x'y'$ polarization selects excitations of pure B_{1g} sym-

metry; at $x'x'$ A_{1g} and B_{2g} excitations may be seen. For simplicity and since phonons of B_{2g} symmetry do not exist in HTSC's we will use only A_{1g} in the following.

Normal-state Raman spectra of Tl 2:2:0:1 at the B_{1g} and the A_{1g} symmetry are shown in Fig. 1 and Fig. 2, respectively. Like in all other HTSC compounds investigated so far the spectra consist of an almost flat continuum and superimposed phononic structures. The continuum extends up to at least 8000 cm^{-1} and is therefore attributed to electronic excitations.

The origin of these excitations will be studied first. To this end, in addition to arguments given earlier,[5] the energy-loss (Stokes) spectra will be compared with the energy-gain (anti-Stokes) spectra. For inelastic scattering far away from resonantly enhanced transitions the intensities should obey the principle of detailed balance,[8]

$$I_{AS}(\omega)=I_{ST}(\omega)\left[\frac{\omega_{AS}}{\omega_{ST}}\right]^2 e^{-\hbar\omega/kT} \quad (1)$$

with $\omega_{ST\,(AS)}$, ω, and T being the absolute frequency of the (anti-)Stokes light, the frequency of the elementary excitation (Raman shift), and the temperature, respectively. In fact, the Stokes and the anti-Stokes spectra of Tl 2:2:0:1 fit excellently at all temperatures using Eq. (1) (Fig. 1). With the temperature as the only fitting parameter the obtained heating is in agreement with the one calculated on the basis of the thermal conductivity as in Tl 2:2:1:2.[9] Therefore, a significant contribution from either recombination scattering (luminescence) or the resonance Raman effect seems unlikely. A contribution from impurity phases can, of course, not be ruled out, but is believed to be small, since related phonon lines are not found. We conclude that the continuum originates predominantly in spontaneous Raman scattering from carriers and analyze the spectra in terms of linear response theory relating the scattering cross section to the absorptive part of the density-density correlation function $\chi''(q,\omega)$.[10] On this basis we find a carrier relaxation rate $\hbar/\tau$ for the normal state which is temperature independent and in the range between 200 and 400 cm^{-1} for the B_{1g} ($x'y'$ in Fig. 1) symmetry and proportional, even almost equal, to T for the A_{1g} ($x'x'$) symmetry.

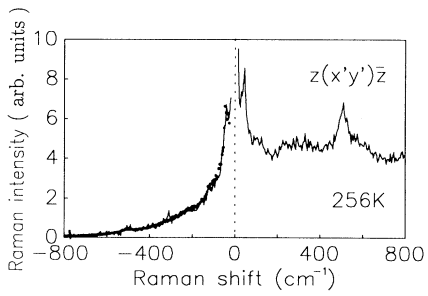

FIG. 1. Anti-Stokes (left) and Stokes (right) spectra for Tl 2:2:0:1 (solid line) at a holder temperature of 250 K. The points on the anti-Stokes side are the best fit of the Stokes to the anti-Stokes spectra using Eq. (1) with the temperature as a fitting parameter. The resulting spot temperature is 256 K.

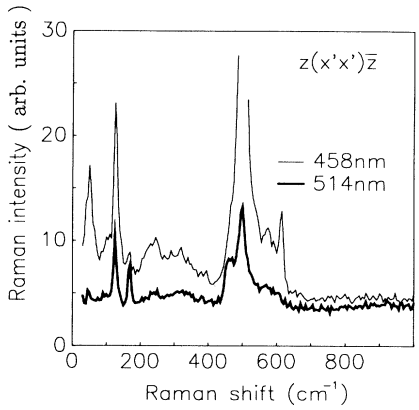

FIG. 2. A_{1g} Raman spectra of Tl 2:2:0:1 for two different excitation wavelengths.

Characteristic changes of the spectral shape occur in the superconducting state [Figs. 3(a) and 3(b)]. For determining the pure electronic scattering the superimposed phononic part consisting of narrow lines and broad structures has to be removed. The resulting peak maxima of the pure electronic contribution are at approximately 450 and 290 cm^{-1} for the B_{1g} and the A_{1g} symmetry, respectively [Fig. 3(c) and 3(d)]. The spectral shape and the peak positions at 20 K are independent of the excitation wavelength.

The interpretation of the superconducting electronic spectra will rest on BCS arguments which have been developed in the past three decades.[11] In these calculations the extreme clean limit is considered with the electronic relaxation rate $\hbar/\tau$ much smaller than the gap energy Δ, thus neglecting the finite lifetime of the electrons. As a consequence the scattering intensity in the normal state is predicted to cut off above a few ten wave numbers in disagreement with experimental observations; as

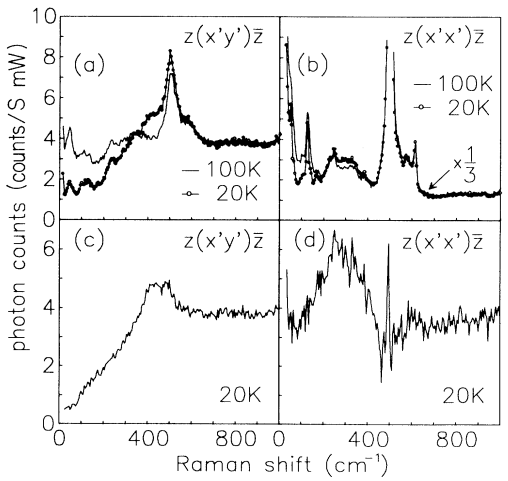

FIG. 3. (a),(b) Raman spectra for Tl 2:2:0:1 just above and well below T_c. The polarizations and the temperatures are indicated. (c),(d) Electronic contribution to the total scattering intensity at $T=20$ K.

shown above for Tl 2:2:0:1 $\hbar/\tau$ is of the same order of magnitude as the expected Δ, and an electronic continuum is found in the whole energy range experimentally accessible. Recently, the Raman spectra for a metal with impurities have been calculated for both the normal[12] and the superconducting state.[13] The obtained result is realistic for the low-energy part of the B_{1g} response in HTSC's, but fails to account for the high intensity at frequency shifts larger than 1000 cm^{-1}. Thus, we have to limit ourselves to a qualitative analysis of the data. For an isotropic material with $\hbar/\tau \leq \Delta$ the peak position is expected to be near 2Δ, which, in this case, may be interpreted as the gap energy or the pair breaking threshold. In the more general anisotropic case the peak frequency approximately reveals the maximum binding energy of the Cooper pairs.[14] For Tl 2:2:0:1 we certainly deal with the latter situation, since the scattering intensity in the small frequency is finite and the peak positions for the $x'y'$ and the $x'x'$ symmetry differ by some 40%. In units of $kT_c = 48...56$ cm^{-1} the peak maxima are between 8 and 9 for the B_{1g} and between 5 and 6 for the A_{1g} symmetry, i.e., at the highest values observed so far in HTSC's.[6,15] Similarly large energies have been found recently for the triple-layer compound[16] demonstrating their intrinsic nature for the Tl family. Unlike in Bi 2:2:1:2 exhibiting a real gap at the B_{1g} symmetry[15] the $\omega=0$ cross section in Tl 2:2:0:1 is nonzero at all polarizations, complicating the discrimination between intrinsic and impurity induced effects. By analogy we may conclude that finite intensity is intrinsic at least at the A_{1g} symmetry. Because of the large superconducting transition width the slope of the spectra below the maximum pair breaking energy, which would be specific for a certain type of anisotropy, cannot provide information in a useful way. In any case, the symmetry properties of the response function require $\chi''(-\omega) = -\chi''(\omega)$, and any frequency dependence of the intensity which is not antisymmetric, specifically finite intensity at $\omega=0$, demands attention per se.

In the following section we briefly address the phonons. Factor group analysis predicts four fully symmetric phonons which have already been observed experimentally.[17] In satisfactory agreement with lattice dynamical calculations[18] we believe them to be the lines at 127, 169, 500, and 603 cm^{-1} observed at the $x'x'$ (Fig. 2) and xx polarization (see Table I). Here an additional line is found at 51 cm^{-1}. The mode at 500 cm^{-1} believed to be A_{1g} violates the selection rules by showing considerable intensity at the xy polarization. The broad bands between 200 and 400 cm^{-1} and 500 and 600 cm^{-1} are observed at all main polarizations, however, with slightly varying intensities. At $x'y'$ we find phonon lines with Lorentzian shape at 45 and 504 cm^{-1} which we believe to be definitely shifted with respect to the modes at 51 and 500 cm^{-1}. Except for the line at 169 cm^{-1} the intensity of all modes is strongly enhanced with the excitation at 458 nm, while the influence of the incoming frequency on the electronic continuum is modest, though not negligible. The lines at 45, 51, and 603 cm^{-1} are particularly weak using green light.

The A_{1g} modes have been assigned to Ba, Tl, and O vibrations along the c axis in the order of increasing energy.[19] According to theoretical[20] and experimental[19] results some mode mixing should occur and particularly the apex oxygen [O(2)] and the oxygen in the Tl-O double layers [O(3)] are not expected to vibrate independently, hence the lines at 500 and 603 cm^{-1} may be in-phase and out-of-phase vibrations of O(2) and O(3) rather than independent O(2) and O(3) vibrations, respectively, as similarly suggested for the Bi family.[21] Strong support for this view comes from the almost identical intensity variation of these lines upon excitation wavelength, which should be indeed similar when the same electronic subsystem or the same bonds are modulated by the movement of the ions. For this reason we conjecture that the phonon lines at 45, 51, and, unlike assumed earlier, at 127 cm^{-1} originate in vibrations with Tl atoms involved predominantly. Then in-phase and out-of-phase vibrations of the Tl parallel to the planes should exhibit the lowest frequencies due to a bond length of roughly 3 Å, whereas the Tl vibration along the c axis is to be expected at a considerably higher energy for the smaller bond length of only 2 Å perpendicular to the planes. Because of the reduced symmetry of the Tl-O layers such vibrations may indeed become Raman active and show up at the indicated polarizations. The broad bands at 200–400 and 500–600 cm^{-1} depend in a similar way on the excitation wavelength and are therefore most naturally identified as in-plane O(3) and out-of-plane O(2)-O(3) vibrations as in the Bi compounds.[21] Particularly the modes between 200 and 400 cm^{-1} which should not be Raman active in a tetragonal unit cell are seen at all polarizations, even if the intensity varies slightly. In Bi 2:2:1:2, on the other hand, with long-range order in the Bi-O layers leading to the well-known orthorhombic distortion of the unit cell, these phonons have pure A_g symmetry.[21] Therefore the additional modes are due to randomly shifted atoms in the Tl-O layers and due to a reduced, but not destroyed translational symmetry in the Bi system. In addition, the disorder in the Tl-O layer may be responsible for the violation of the A_{1g} selection rule which is particularly strong for the phonon at 500 cm^{-1}. In contrast to the other modes the line at 169 cm^{-1} is much stronger with green excitation. This may be an indication of mainly Ba atoms being involved in this phonon thus being in disagreement with the formerly favored

TABLE I. Peak frequencies of prominent Raman lines for Tl 2:2:0:1 at the main polarizations. The symmetry-allowed modes are printed boldface. Polarizations not measured at 514 nm and marked by asterisk.

	$x'y'$			$x'x'$				xy		xx			
458 nm	45	505	51	**127**	**169**	**500**	**603**	500	51	**127**	**169**	**500**	**603**
514 nm		503		**127**	**169**	**500**		*			*		

assignment.[16,20]

To summarize, we have observed the four A_{1g} phonons predicted by factor group analysis for Tl 2:2:0:1 and several additional lines and bands which are most likely induced by disorder in the Tl-O layers. A final assignment of the observed modes, however, is still not possible. According to the dependence of the phonon intensity on the excitation frequency it seems more likely that the line at 127 cm^{-1} originates in Tl and the one at 169 cm^{-1} in Ba vibrations. We conjecture that the new modes found at 45 and 51 cm^{-1} come from in-plane vibrations of the heavy Tl atoms.

Superconducting gap excitations have been measured in single-layer Tl 2:2:0:1 and reveal a maximum binding energy of the pairs between 8 and 9 kT_c. The electronic scattering in Tl 2:2:0:1 compares well to the one observed in $YBa_2Cu_3O_7$ and in $Bi_2Sr_2CaCu_2O_8$.[6,15] Clearly, the selection rules are determined by the orientation of the Cu-O bonds in the planes as shown most strikingly by the polarization dependence of the superconducting structures, but also by the carrier relaxation in the normal state. The normalized maximum binding energies at the B_{1g} symmetry $2\Delta/kT_c$ increase almost proportionally to the maximum T_c of 93, 110, and 125 K obtainable in the Y, the Bi, and the Tl families, respectively, obeying approximately $2\Delta/kT_c=\alpha T_c^{\max}$ with the constant $\alpha=0.07$ K^{-1}. Along with the large values this may be an indication of strong coupling.

We would like to thank M. P. Kulakov for providing single crystals of $Tl_2Ba_2CuO_6$ and N. Nücker for cutting the crystal used here with the ultramicrotome. We are particularly indebted to H. Veith for determining the superconducting parameters of our sample. One of us (O.V.M.) acknowledges support from the Alexander-von-Humbolt Foundation and expresses his gratitude for the hospitality at the Walther-Meissner-Institut für Tieftemperaturforschung. The work has been supported by the Bayerische Forschungsstiftung via the Forschungsverbund Hochtemperatur-Supraleitung (FORSUPRA).

*Present and permanent address: Institute of Solid State Physics, Academy of Sciences of Russia, 142432 Chernogolovka, Russia.

[1]N. N. Kolesnikov, V. E. Korotkov, M. P. Kulakov, R. P. Shibaeva, V. N. Molchanov, R. A. Tamaz'yan, and V. I. Simonov, Physica C (Amsterdam) **195**, 219 (1992).

[2]T. Zetterer, M. Franz, J. Schützmann, W. Ose, H. H. Otto, and K. F. Renk, in *Electronic Properties of High Temperature Superconductors and Related Compounds,* edited by H. Kuzmany, M. Mehring, and J. Fink (Springer, Berlin, 1990); T. Zetterer, Doctoral thesis, Universität Regensburg, 1990 (unpublished).

[3]Y. Shimakawa, Y. Kubo, T. Manako, and H. Igarashi, Phys. Rev. B **40**, 11400 (1989); C. Allgeier, Doctoral thesis, Universität München, 1990 (unpublished).

[4]O. M. Vyaselev, N. N. Kolesnikov, M. P. Kulakov, and L. F. Schegolev, Physica C (Amsterdam) **199**, 50 (1992).

[5]T. Staufer, R. Hackl, and P. Müller, Solid State Commun. **75**, 975 (1990); **79**, 409 (1991).

[6]R. Hackl, W. Gläser, P. Müller, D. Einzel, and K. Andres, Phys. Rev. B **38**, 7133 (1988).

[7]R. Hackl, Doctoral thesis, Technische Universität München, 1987 (unpublished).

[8]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960).

[9]A. A. Maximov, A. V. Puchkov, I. I. Tartakovskii, V. B. Timofeev, D. Reznik, and M. V. Klein, Solid State Commun. **81**, 407 (1992).

[10]D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, London, 1975).

[11]H. Monien and A. Zawadowski, Phys. Rev. B **41**, 8798 (1990), and references therein.

[12]A. Zawadowski and M. Cardona, Phys. Rev. B **42**, 10732 (1990).

[13]T. P. Devereaux, Phys. Rev. B **45**, 12965 (1992); Phys. Rev. B (to be published).

[14]D. Einzel (private communication).

[15]T. Staufer, R. Nemetschek, R. Hackl, P. Müller, and H. Veith, Phys. Rev. Lett. **68**, 1069 (1992).

[16]Data for the xx polarization have been obtained by M. C. Krantz, H. J. Rosen, J. Y. T. Wei, and D. E. Morris, Phys. Rev. B **40**, 2635 (1989); the $x'x'$ and the $x'y'$ symmetries have been studied by B. Stadlober and R. Hackl (unpublished).

[17]M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 11962 (1988).

[18]A. D. Kulkarni, F. W. de Wette, J. Prade, and W. Kress, Phys. Rev. B **43**, 5451 (1991).

[19]L. V. Gasparov, O. V. Misochko, M. I. Eremets, E. S. Itskevich, A. V. Lomsadze, V. V. Struzhkin, and A. M. Shirokov, Solid State Commun. **72**, 465 (1989).

[20]E. I. Rashba and E. Ya. Sherman, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 404 (1988) [JETP Lett. **47**, 482 (1988)]; O. V. Misochko and E. Ya. Sherman, Supercond: Phys. Chem. Technol. **3**, 2524 (1990).

[21]P. Knoll, B. Stadlober, and N. Brnicevic, Physica C (Amsterdam) **162–164**, 1097 (1989); B. Stadlober, Diploma thesis, Universität Graz, 1991 (unpublished).