Pseudogap and Superconducting Gap in the Electronic Raman Spectra of Underdoped Cuprates

R. Nemetschek, M. Opel, C. Hoffmann, P. F. Müller, and R. Hackl
Walther Meissner Institut, Bayerische Akademie der Wissenschaften, D-85748 Garching, Germany

H. Berger and L. Forró
Ecole Polytechnique Fédérale de Lausanne, Ecublens, CH-1015 Lausanne, Switzerland

A. Erb and E. Walker
DPMC, Université de Genève, CH-1211 Genève, Switzerland
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Raman spectra of $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2(Ca_{0.62}Y_{0.38})Cu_2O_{8+\delta}$ with $T_c \cong 0.65T_c^{\max}$ in the underdoped regime of the phase diagram are studied as a function of temperature and polarization. At B_{2g} (xy) symmetry a reduction of spectral weight by 10% for frequencies less than 700 cm^{-1} or $15k_BT_c$ is found below approximately 200 K. Below T_c, a superconducting gap opens up which closely resembles that observed at higher doping levels. It is compatible with $d_{x^2-y^2}$ pairing and its amplitude $2\Delta_0$ can be estimated to be $8k_BT_c$. [S0031-9007(97)03387-5]

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The doping-temperature phase diagram of all CuO_2 systems shows the proximity of magnetically ordered, metallic, and superconducting phases, and suggests that these phases are all interrelated. The undoped parent compounds are antiferromagnetically (AF) ordered Mott-Hubbard insulators, and magnetic fluctuations are observed along with superconductivity at low doping levels. Therefore, the evolution of the metallic phase from the AF insulating phase attracted a great deal of attention. Recently, gaplike features in the electronic spectrum of underdoped cuprates have been inferred from or directly observed in measurements of the specific heat [1], the dc [2], and infrared (ir) [3] conductivity, and in angle-resolved photoemission (ARPES) experiments [4] at characteristic temperatures T^* well above T_c. Although several ideas have been proposed which can lead to a qualitative understanding of this phenomenon [5–12], at present the interpretation of, and the relationship between, these results is not settled. In part, this is related to not yet understood discrepancies in the experimental data obtained by different methods. In addition, basically all experimental techniques used so far are not similarly sensitive to both the formation of the pseudogap at T^* and the transition to the superconducting phase at T_c which is expected to develop a full, though most likely, strongly **k**-dependent gap.

In this Letter, we want to contribute new information obtained from inelastic light-scattering experiments as both types of gaps can clearly be identified in the spectra. So far, only the superconducting gap could be found by Raman scattering [13]. All observations pointed to a strong anisotropy in **k** space and a superconducting order parameter which is most compatible with $d_{x^2-y^2}$ pairing [13,14]. In the normal state the electronic response is also related to carrier properties [13]. Then, anomalies such as a pseudogap which are observed in the conductivity [3] should manifest themselves in the Raman spectra. In addition to what is found in ir experiments, Raman scattering weighs out different parts of the Fermi surface (FS) for different light polarizations, and therefore anisotropies may be studied. The purpose of this paper is to demonstrate the direct observation of the pseudogap and, at lower temperatures, that of the superconducting gap in the Raman spectra of underdoped cuprates, and to discuss the dependences on polarization, energy, and temperature.

The experiments were performed in back-scattering geometry using a standard Raman setup with excitation at 476 nm, a spot size of 50×150 μm^2, and laser powers between 0.3 and 4 mW. The polarizations of the incoming and outgoing photons were always parallel to the CuO_2 planes. All symmetries refer to a tetragonal point group. We studied single crystals of $Bi_2Sr_2(Ca_{0.62}Y_{0.38})Cu_2O_{8+\delta}$ (Bi2212) and $YBa_2Cu_3O_{7-x}$ (Y123). Bi2212 was prepared in ZrO crucibles. The resistively determined T_c (midpoint) is 57 K, the width is $\Delta T_c = 5$ K. The Y123 crystal was grown in $BaZrO_3$ [15], annealed for 100 h at 784 °C in 1 bar oxygen, and subsequently quenched. According to the calibration by Lindemer *et al.*, this thermal treatment results in an oxygen content of 6.5 [16]. The magnetically measured transition temperature is $T_c = 53.5$ K with $\Delta T_c = 3$ K. It is important to note that in Y123 the actual T_c relevant to the Raman experiment can be higher by several degrees due to the illumination with intense light [17]. Therefore a higher approximate value for T_c is given in the figures.

The underdoped materials exhibit an important difference to samples with optimal or higher doping levels in that features related to properties of the carriers can be observed only at B_{2g} polarization. At the other two symmetries, A_{1g} and B_{1g}, the spectra show hardly any temperature dependence [18]. Therefore we will discuss here B_{2g} data only.

The normal state response $\mathrm{Im}\chi(\omega, T)$ for three differently doped Bi2212 samples is plotted for various temperatures in Fig. 1. Panels (a) and (b) are shown only for comparison and are reproduced here from earlier work [13,19]. All spectra consist of slowly varying continua and superimposed narrow structures due to phonons. To clarify the evolution of the spectra with temperature, we focus first on the optimally doped sample [Fig. 1(b)]. Upon cooling, the slope $\partial \mathrm{Im}\chi/\partial\omega$ close to $\omega = 0$ increases continuously. Above some 800 cm^{-1}, all spectra merge together and do not exhibit any systematic temperature dependence. Essentially the same behavior of the continuum is found for the overdoped sample [Fig. 1(a)]. The underdoped material [Fig. 1(c)] exhibits a similar variation with temperature down to some 200 K. Then, as a new feature, spectral weight is lost below 700 cm^{-1} while the slope at low energies continues to increase. Between 250 and 700 cm^{-1}, the spectrum at 80 K is roughly 10% below those at high temperatures. The very same variation with temperature is found for underdoped Y123 (Fig. 2). For both materials the temperature dependence of the integrated spectral weight is plotted in Fig. 3. The integration limits are set as indicated in Figs. 1(c) and 2, and cut off the low-energy parts with trivial temperature dependence [see Figs. 1(a) and 1(b)]. In each case, the depletion of spectral weight starts at approximately 200 K and tends to saturate at about 100 K. If it exists at all in optimally doped Bi2212, the reduction of weight is much smaller and is shifted to lower temperatures [Fig. 3(a)].

In the superconducting state, additional structures appear in the spectra which peak at 230 ± 10 cm^{-1} (light lines in Fig. 4). They have completely similar shapes as those found in optimally doped and overdoped samples at the same symmetry [14,18]. Accordingly, they are interpreted as a signature of coherent pair formation and of a superconducting energy gap. The peak intensity is particularly big for Y123, highlighting the extreme purity of this material [15,20]. At low energies the intensities now vary linearly over almost a decade which clearly contrasts the convex curvature apparent at all temperatures above T_c.

We first briefly address the surprising observation that carrier properties are found only at B_{2g} symmetry. Changes of the A_{1g} and B_{1g} intensities relative to the B_{2g} intensity upon doping have already been found in $La_{2-x}Sr_xCuO_4$ [21] and Y123 [22]. We propose an interpretation in terms of the Raman vertices $\gamma^{\mu}(\mathbf{k})$, which determine the $\mathbf{k}$ dependence of the sensitivity. Useful first order expansion functions of $\gamma^{\mu}(\mathbf{k})$ on a tetragonal lattice are given by $(\cos k_x - \cos k_y)$, $(\sin k_x \sin k_y)$, and $(\cos k_x + \cos k_y)$ for the three symmetries $\mu = B_{1g}, B_{2g}$, and A_{1g}, respectively, being Raman active for in-plane polarizations. At $(\pi/2, \pi/2)$ both the A_{1g} and the B_{1g} vertices are zero while B_{2g} is maximal. Now, if the FS is confined to the vicinity of $(\pi/2, \pi/2)$ or if the electronic spectral function is suppressed close to the principal axes as can be expected in underdoped cuprates due to correlation effects [8,23] or strong electron-spin interactions

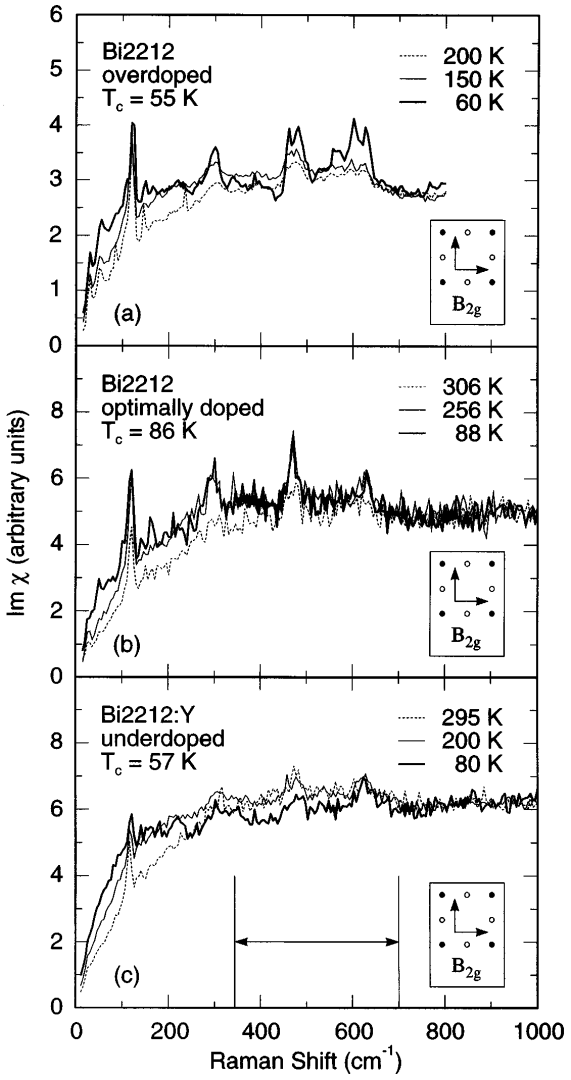

FIG. 1. (a)–(c) Raman response functions $\mathrm{Im}\chi(\omega, T) \cong [1 - \exp(-\hbar\omega/k_BT)](\partial^2\sigma/\partial\omega\,\partial\Omega)$ of differently doped Bi2212 single crystals at B_{2g} symmetry in the normal state at experimentally determined spot temperatures. The polarizations of the incoming and outgoing light are given with respect to the copper (solid circles) and oxygen (open circles) planes. In panel (c) the range is indicated in which the intensity is integrated for Fig. 3.

[10], respectively, the scattering from carriers should be much weaker in the A_{1g} and B_{1g} spectra. The remaining almost temperature independent intensities may come in part from spin excitations which are strongly suppressed in B_{2g} symmetry and projected out at B_{1g} and at A_{1g} polarizations [24].

In the superconducting state we observe the B_{2g} intensity to increase linearly with frequency with an intercept very close to zero (Fig. 4). Therefore an isotropic gap can safely be excluded. Moreover, the shapes shown in Fig. 4 are similar to those predicted theoretically for a gap with $d_{x^2-y^2}$ symmetry [14]. In units of k_BT_c, the B_{2g} pair-breaking maxima are found at the same position as for all other doping levels and material classes [13,18,25]. Consequently, even without the information from the other

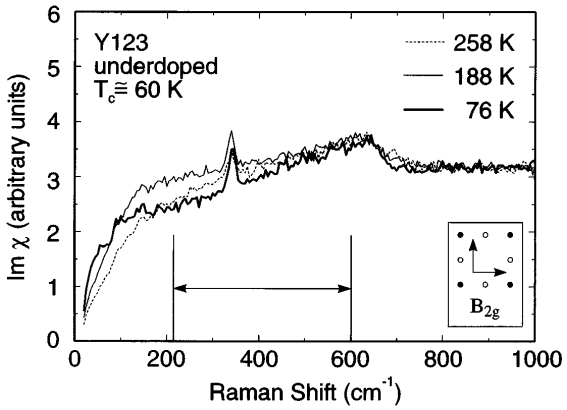

FIG. 2. Raman response for underdoped Y123. The arrows indicate the integration range for the determination of the spectral weight displayed in Fig. 3.

channels it is most likely that the superconducting state has essentially the same properties at low doping as at higher doping levels, i.e., predominantly $d_{x^2-y^2}$ symmetry.

Above T_c the low-frequency part of the spectra immediately assumes a convex shape. This shape is observed for all temperatures and doping levels studied (Figs. 1 and 2). In the most plausible scenario the response is then collision limited and can be described by a Drude-like kernel [26], $\mathrm{Im}\chi_{\mathbf{k}}(\omega) = -\varphi_{\mathbf{k}}\omega\tau_{\mathbf{k}}/[1 + (\omega\tau_{\mathbf{k}})^2]$. Here $\varphi_{\mathbf{k}}$ is the derivative of the equilibrium distribution function with respect to the quasiparticle energy and is proportional to the density of levels at a given $\mathbf{k}$. $\tau_{\mathbf{k}}$ is a characteristic relaxation time [13]. In fact, the low-frequency part of the spectra is well described by this function at all temperatures. This implies that above T_c the B_{2g} response at small frequencies is indistinguishable from that of an ordinary metal with the finite lifetime of the carriers in complete agreement with ir measurements [3]. In particular, in (π, π) direction there is neither a nodal structure, since the characteristic linear variation of the response as observed, for instance, in the superconducting state is missing, nor a finite gap which would manifest itself as a threshold in the spectrum. Hence, for an explanation of the missing spectral weight below 700 cm^{-1} and the simultaneously occurring metallic behavior at $\omega \to 0$, we have to invoke a reduced or vanishing density of electronic states at the Fermi energy ε_F away from the diagonals in the vicinity of the principal axes and, around the diagonals, extended areas on the FS with finite density of states. Up to this point, Raman and ARPES [4] results are compatible. It is found here, however, that the details of the variation with $\mathbf{k}$ and the energy scales are substantially different for the two quantities. This means that

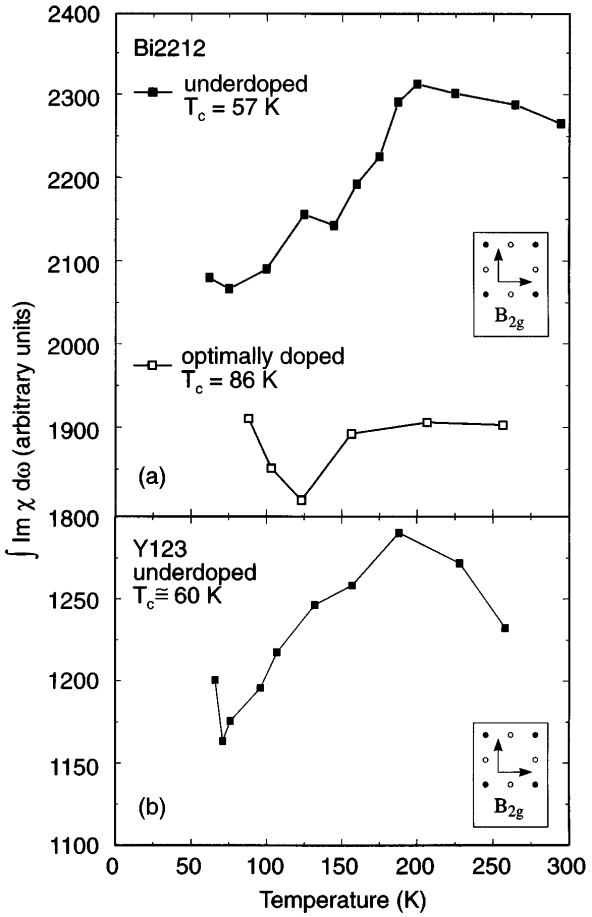

FIG. 3. Spectral weight of the B_{2g} spectra of optimally and underdoped Bi2212 (a) and underdoped Y123 (b) as a function of temperature.

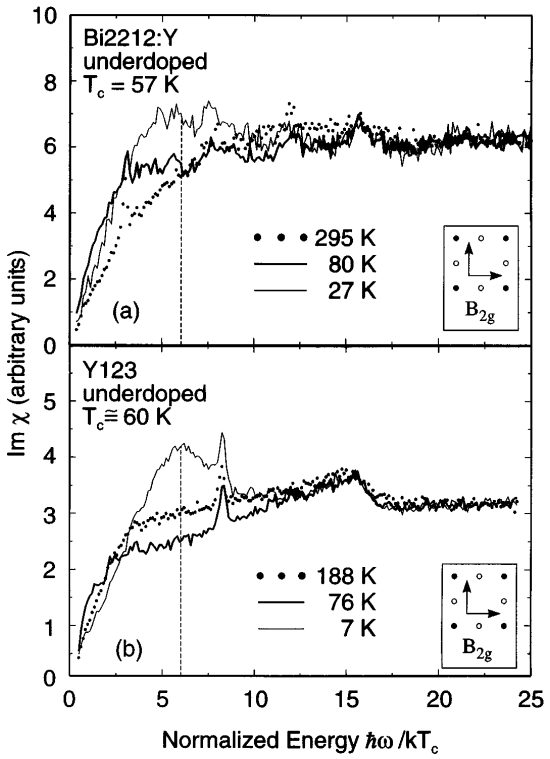

FIG. 4. Raman response functions of underdoped (a) Bi2212 and (b) Y123 at temperatures above and below T_c. $k_B T_c$ is approximately 40 cm^{-1}. The T_c indicated for Y123 (b) is higher than that measured magnetically according to what is expected for underdoped samples under intense light [17]. Close to this temperature, the pair-breaking feature disappears.

there exist two different types of gaps exhibiting a similar phenomenology as found in superconducting spin or charge density wave systems.

The B_{2g} spectra do not project out the maxima of the two observed gaps as the respective Raman vertex vanishes along $(\pi, 0)$. The full energy scale might be larger by a factor up to 1.5 [14]. Then the amplitude of the superconducting gap is of the order of 8 in units of $k_B T_c$ and that of the pseudogap is at least twice as large. This energy is close to the exchange energy J and is much larger than that of the spin gap found by inelastic neutron scattering [27]. The pseudogap starts to open up at the same temperature, where anomalies are found in the ^{63}Cu spin-lattice relaxation rate in NMR [28] and in the phonon spectrum [29].

The idea of a normal state gap in the cuprates was proposed very early [5] and pursued in the t-J model [7,8]. A similar reduction of electronic states above T_c is also predicted in the spin bag [12] and the nearly AF-Fermi-liquid scenario [10]. The existence of preformed incoherently moving pairs in the normal state below T^* which develop a uniform phase [6,9,11] at the superconducting transition would also lead to the reduction of states close to the Fermi edge in the temperature range between T^* and T_c. It is, however, noted that the Raman results presented here show different magnitudes for the two types of gaps.

In summary, we have studied the in-plane Raman response in underdoped single crystals of Y123 and Bi2212 with $T_c \cong 0.65 T_c^{\max}$. In both compounds it is found consistently that carrier-related properties are predominantly seen at the B_{2g} symmetry. This can be interpreted straightforwardly if one invokes the formation of FS pockets at $(\pi/2, \pi/2)$ or a strong suppression of the electronic spectral function close to $(\pi, 0)$ at this doping level. Below 200 K, a pseudogap opens up in the carrier channel for frequencies less than approximately 700 cm^{-1} which goes along with a reduction of the spectral weight by 10%. As the energy scale is comparable to that of the exchange interaction J, one might speculate that the driving force is magnetic. At the superconducting transition, additional features appear which are interpreted in terms of pair breaking and the opening of a superconducting gap. The energy of the pair-breaking peak is $6 k_B T_c$ which is the same as in optimally doped and overdoped cuprates. Mainly due to the linear increase of the intensity at $T \to 0$, it can be concluded that the gap has predominantly $d_{x^2-y^2}$ symmetry.

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[1] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993).
[2] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).
[3] A. V. Puchkov *et al.*, Phys. Rev. Lett. **77**, 3212 (1996), and references therein.
[4] A. G. Loeser *et al.*, Science **273**, 325 (1996).
[5] P. W. Anderson, Science **235**, 1196 (1987).
[6] V. Emery and S. A. Kivelson, Nature (London) **374**, 434 (1995).
[7] H. Fukuyama and H. Kohno, Czech. J. Phys. **46**, Suppl. S6, 3146 (1996).
[8] P. A. Lee, J. Low Temp. Phys. **105**, 581 (1996).
[9] N. F. Mott, Philos. Mag. Lett. **63**, 319 (1991).
[10] D. Pines, Physica (Amsterdam) **163B**, 78 (1990); Z. Phys. B (to be published).
[11] J. Ranninger and J. M. Robin, Phys. Rev. B **53**, R11 961 (1996).
[12] J. R. Schrieffer and A. P. Kampf, J. Phys. Chem. Solids **56**, 1673 (1995).
[13] D. Einzel and R. Hackl, J. Raman Spectrosc. **27**, 307 (1996).
[14] T. P. Devereaux *et al.*, Phys. Rev. Lett. **72**, 396 (1994); T. P. Devereaux and D. Einzel, Phys. Rev. B **51**, 16 336 (1995).
[15] A. Erb, E. Walker, and R. Flükiger, Physica (Amsterdam) **245C**, 245 (1995).
[16] T. B. Lindemer *et al.*, J. Am. Ceram. Soc. **71**, 1775 (1992).
[17] E. Osquiguil *et al.*, Phys. Rev. B **49**, 3675 (1994).
[18] R. Hackl *et al.*, J. Low Temp. Phys. **105**, 733 (1996).
[19] M. Opel, diploma thesis, Technical University Munich, 1995 (unpublished).
[20] T. P. Devereaux, Phys. Rev. Lett. **74**, 4313 (1995).
[21] T. Katsufuji *et al.*, Phys. Rev. B **48**, 16 131 (1993).
[22] X. K. Chen *et al.*, Physica (Amsterdam) **227C**, 113 (1994); (to be published).
[23] D. S. Marshall *et al.*, Phys. Rev. Lett. **76**, 4841 (1996).
[24] K. B. Lyons *et al.*, Phys. Rev. Lett. **60**, 732 (1988); M. Pressl *et al.*, J. Raman Spectrosc. **27**, 343 (1996); M. Rübhausen *et al.*, J. Low Temp. Phys. **105**, 761 (1996).
[25] C. Kendziora and A. Rosenberg, Phys. Rev. B **52**, 9867 (1995); these authors did not find any pair-breaking features in B_{2g} symmetry in underdoped samples but rather a structure in B_{1g} symmetry, the frequency of which increases with decreasing doping level [see also F. Slakey *et al.*, Phys. Rev. B **42**, 2643 (1990)]. In none of the underdoped samples we studied could such a B_{1g} peak be observed, in particular, not above T_c. Rather we observed a B_{2g} structure which disappeared at $T_c \pm \Delta T_c$. The intensity of this structure is directly proportionate to the sample purity (see [20]).
[26] A. Zawadowski and M. Cardona, Phys. Rev. B **42**, 10 732 (1990).
[27] J. Rossat-Mignod *et al.*, Physica (Amsterdam) **185C–189C**, 86 (1991).
[28] T. Imai *et al.*, Physica (Amsterdam) **162C–164C**, 169 (1989).
[29] A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).