Electronic Raman Scattering and Phonon Self-Energy Effects in the RE-123 System: Signatures of Gap and Pseudogap

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Using Raman spectroscopy and transport measurements we investigate thin epitaxial films of Y_{1−x}(Pr,Ca)$_x$Ba$_2$Cu$_3$O$_{6+y}$. We explore the electronic Raman responses in $A_{1g}$, $B_{1g}$, and $B_{2g}$ symmetry obtained after subtraction of phononic excitations, and especially, the $2\Delta$ peaks that form out of the electronic background below $T_c$. We find that the energy of the $B_{1g}$ $2\Delta$ peak, which is a measure of the gap value, increases monotonically with decreasing doping until the peaks become unresolvable. In contrast, the peaks in $A_{1g}$ symmetry follow $T_c$ being still resolvable in the Pr-doped films. The $B_{2g}$ responses are weak and a $2\Delta$ peak is only detected at the highest doping level. As a consequence of strong electron-phonon coupling, the $B_{1g}$ phonon at $\sim 340$ cm$^{-1}$ exhibits a pronounced Fano-type line shape. We use a phenomenological model to describe the line shape that takes into account real and imaginary part of the electronic response. It allows us to obtain the self-energy corrections and the mass-enhancement factor $\lambda$ as a measure of the coupling. In the normal state we find $\lambda = 0.015$ around optimal doping and decreasing values with decreasing doping. The electron-phonon coupling increases strongly below $T_c$ in overdoped samples in which the $B_{1g}$ $2\Delta$ peaks appear in the vicinity of the phonon. Self-energy effects observed in the superconducting state can only partly be assigned to the redistributing electronic response. Anomalies with respect to frequency, linewidth, and intensity remain. They appear at increasing temperatures with decreasing doping and we provide evidence that they are connected to the presence of a pseudogap.

We supplement our study by a comparison with single crystal data and investigate the influence of site-substitutional disorder on the electronic response and the electron-phonon interaction.

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I. INTRODUCTION

Since the discovery of the cuprate high-temperature superconductors (HTS) it has been established that the important common feature of all cuprates are the copper-oxygen (CuO$_2$) planes. Even though not discovered yet, it is believed that the mechanism causing the high transition temperatures $T_c$ is located in and related to these planes. Often discussed candidates for the pairing mechanism are an exchange of antiferromagnetic fluctuations or interlayer tunneling. The role phonons play in the mechanism is not resolved. Isotope experiments indicate that phonons may be involved at least away from optimal doping which is defined by $\sim 0.16$ holes per plane in the unit cell. However, the observed and calculated electron-phonon couplings are too small to explain $T_c$’s above $\sim 50$ K. Nevertheless, it is noted that the electron-phonon coupling in the cuprate HTS is another example of their exotic properties.

Difficult to understand in the framework of phonon-mediated pairing are the various peculiarities of the superconducting gap that have been established so far. The most important one concerns its symmetry which appears to be predominantly of $d_{xy}$-$d_{x^2-y^2}$-wave type. Others are the strange dependencies of the gap on temperature and on doping observed with various spectroscopic methods like e.g. tunneling, angle-resolved photoemission (ARPES), or Raman spectroscopy. Moreover, it is found that a pseudogap exists in the excitation spectra of underdoped cuprates above $T_c$. Recent ARPES studies indicated that gap and pseudogap are intimately related. In detail, it was observed that in underdoped compounds a gap opens up at the Fermi surface (FS) crossings along the $(\pi, 0)$ to $(\pi, \pi)$ directions at the pseudogap temperature $T^*$. Below that temperature the gapped regions grow continuously, covering the entire FS at $T_c$. However, recent scanning tunneling microscopy measurements indicated an increasing pseudogap above $T_c$ which disappeared close to room temperature independent of doping. An intimate relation of both gaps is predicted in the precursor scenario as presented by Emery and Kivelson in which preformed pairs exist above the transition temperature but no phase coherence between the pairs is established. Both gaps are assumed to be unrelated in scenarios in which the pseudogap is associated with competing magnetic or charge density wave instabilities.

Even though $T_c$ exhibits a maximum at optimal doping, various spectroscopies revealed that the gap near $T = 0$ increases in a monotonic fashion with decreasing doping. This behavior contradicts with mean-field pictures according to which the ratio $2\Delta(T = 0)/k_BT_c$ should be constant. The behavior is, however, in agreement with pictures in which $T_c$ in the underdoped regime is regarded as the temperature of a Bose-Einstein condensation of preformed pairs. In the latter case the
increasing gap energy with decreasing doping can be related to the concomitantly increasing strength of the antiferromagnetic correlations and the decreasing $T_c$ to the decreasing density of Cooper pairs. Whereas gap features are observed in tunneling and ARPES spectroscopy at all dopings, the $2\Delta$ peaks measured in Raman spectroscopy diminish strongly in the underdoped region of the phase diagram. The temperature dependence of the $2\Delta$ peaks is weak and commonly they vanish above $T_c$. However, recently a small doping-independent feature has been reported to persist into the normal state in underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8-\delta}$ (Bi-2212). Indications of the pseudogap in electronic Raman scattering of underdoped cuprate HTS so far, are reductions of spectral weight seen in $B_{2g}$ (Ref. 31) and $B_{1g}$ symmetry. In addition, anomalies have been observed around $T^*$ with respect to phonon frequencies and intensities of interband electronic excitations. Whereas pseudogap features above $T_c$ are consistently observed by various techniques in the underdoped region of the phase diagram it is currently under debate whether a pseudogap is also present in overdoped compounds.

Using Raman spectroscopy not only electronic but also phononic excitations can be investigated. In this regard, the renormalization of phonons due to the interband electronic excitations is of particular interest. A famous example for these kind of studies is the $B_{1g}$ Raman-active phonon at $\sim 340$ cm$^{-1}$ in REBa$_2$Cu$_3$O$_{7-\delta}$ (RE-123) with RE a rare-earth atom or Y. This phonon represents an out-of-phase vibration of the planar oxygen and couples remarkably strong to electronic excitations. The strength of the coupling is related to the buckling of the CuO$_2$ planes in RE-123 compounds and the $B_{1g}$ phonon is much weaker in compounds in which the planes are flat, e.g. in Bi-2212. Moreover, it was shown that the coupling is amplified by the crystal field originating from the different valences at the RE and the Ba site on both sides of the plane. As the symmetry of the $B_{1g}$ phonon matches that of the order parameter and as its energy is close to $2\Delta$, at least for overdoped RE-123, the $B_{1g}$ phonon turns out to be particularly well-suited for the investigation of the electron-phonon coupling. Neutron experiments have shown that the strongest coupling of this phonon is observed for $q$ along the [100]-direction where the $d_{x^2-y^2}$-wave order parameter has its maximum size. There, the most pronounced self-energy effects are observed in the vicinity of the Brillouin zone center which is probed by Raman spectroscopy.

Due to its coupling to low-energy electronic excitation the $B_{1g}$ phonon has a Fano-type line shape. The change of the line-shape parameters at low temperatures was therefore identified as originating from a superconductivity-induced redistribution of the electronic excitation spectrum. The renormalization of this phonon in various RE-123 polycrystals, in which either the rare-earth atom or the oxygen isotope or both have been substituted in order to shift the phonon frequency, could be accounted for in a strong-coupling theory by Zeyher and Zwicknagl using an $s$-wave symmetry of the order parameter and a mass-enhancement factor $\lambda = 0.02$. Not all Raman experiments could be consistently described within this picture leading to an intensive discussion at that time. More recent theoretical treatments of phonon renormalization have considered $d_{x^2-y^2}$-wave order parameter. The latter theories have confirmed that the matching symmetries of phonon and gap are important to obtain strong phonon renormalizations. The largely varying $2\Delta/k_BT_c$ ratios obtained in the earlier phonon self-energy studies can be accounted for if one not only considers the symmetry but also the strong doping dependence of the superconducting gap.

Except for some recent investigations of mercury or carbonate based four-layer compounds, most of the self-energy studies have been carried out on the RE-123 system. In contrast, $2\Delta$ peaks, which are a signature of pair-breaking excitations, have been investigated in various cuprate families such as the single-layer compounds La$_2$−$x$Sr$_x$CuO$_4$−$\delta$ (Ref. 54) and Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2201) (Ref. 55) or the double-layer compounds Bi-2212 (Ref. 25,56,57) or Y-123 (Ref. 58,59). Above $T_c$, a structureless background is observed in all plane-polarized excitation geometries. The background can be assigned to incoherent quasi-particle scattering. This scattering, which is observed with other spectroscopic methods as well, extends at least up to energy transfers of $\sim 1$ eV. Except for very high dopings, low-temperature Raman spectra of the aforementioned compounds share the following features: (i) The energy of the $B_{1g}$ $2\Delta$ peak exceeds that of the $A_{1g}$ $2\Delta$ peak and increases with decreasing doping. (ii) The intensity of the background features increase with increasing doping.

Recently, various calculations have been presented which allow a description of the low-temperature electronic continuum in different polarization geometries. These theories rely on the approach of Klein and Dierker in which the mass part of the interaction of light with superconducting electrons of a conventional electron gas exhibiting a gap in its excitation spectrum is used. The main features observed in the Raman spectra, such as different energies and power laws in different polarization geometries, can be described within a $d_{x^2-y^2}$-wave picture, at least near optimal doping. However, the relatively strong intensities of the $A_{1g}$ $2\Delta$ peaks, the vanishing intensities of the gap features at low doping levels, and the converging peak energies at high doping levels are only three features that cannot be explained with the present theories. Hence, it appears that the strong electron-electron interactions have to be more thoroughly considered in theoretical descriptions of the Raman spectra.

Whereas previous works focussed either on the gap features or on the phonon self-energy effects, here we investigate how far both effects are correlated. In order to do that we use an extended Fano formula that we have pre-
sent previously that takes into account the real and imaginary parts of the electronic response function and a phenomenological description of the response. This work extends our previous study towards lower dopings and includes investigations of the Raman responses in $A_{1g}$ and $B_{2g}$ symmetry in addition to the ones in $B_{1g}$. The phenomenology that we have presented allows us to obtain measures of the electron-phonon coupling, e.g. via the mass-enhancement factor $\lambda$. Moreover, it enables us to identify the shape of the electronic background in the presence of strongly interacting phonons which is of particular interest.

The investigated epitaxial $Y_{1-x}(Pr, Ca)_x Ba_2Cu_3O_{6+y}$ films cover a wide doping range. To access the under-doped side of the phase diagram we use oxygen reduction as well as Pr substitution. Comparison of both methods allows us to study the influence of broken chains and of additional scatterers close to the CuO$_2$ planes on the Raman response. We also compare the results of ordered samples with others in which site-substitution disorder with respect to a Pr ↔ Ba or a Ca ↔ Ba exchange is present. We complete our study with an investigation of a single crystal.

In addition to the Raman spectra we have studied the transport properties of the films which facilitates a determination of $T_c$ and $T''$. The three main interests of this study are: (i) We want to investigate the doping dependence of the $2\Delta$ peaks in $A_{1g}$ as well as in $B_{1g}$ symmetry in view of the non-mean field behavior of the gap observed in Bi-2212 compounds, paying attention to the influence of disorder on these quantities. (ii) We want to explore the temperature and doping dependence of the electron-phonon coupling and the phonon self-energies at high dopings, when $2\Delta$ approaches the phonon energy, and at low dopings, in the pseudogap regime, when $2\Delta$ peaks in $B_{1g}$ are not observed. At low dopings we are particularly interested to find signatures of the pseudogap. (iii) We want to establish the temperature dependence of the gap energy and investigate whether we find indications for a monotonically closing pseudogap above $T_c$ as observed in ARPES measurements. In our study we benefit from the high temperature accuracies that are achieved when thin films are investigated.

This paper is organized as follows. In Sec. II properties of the investigated films and the single crystal are presented as well as the setups that have been used for the Raman and transport measurements. After a brief recapitulation of the phenomenology used to describe phonons superimposed on an interfering background we will give an example how the data are analyzed in Sec. II A. In Sec. II A the influence of the oxygen content on the electronic background as well as on the phonon self-energy effects in thin films is discussed. Results obtained on a single crystal are given in Sec. II B. The influence of the element substitutions Pr and Ca for Y on the background feature as well as on the phonon self-energy effects is presented in Sec. II C. Whereas in Sec. IVA ordered samples are investigated, Sec. IVB focuses on the effects of site-substitution disorder when the Ba site is substituted in addition to the rare-earth site. In Sec. IVA analyses of Raman and transport data are used to assign particular doping levels to the films and the single crystal. Also the pseudogap temperatures will be determined. Subsequently, in Secs. IVB and IVC we will discuss our results regarding the phonon self-energy effects and the background features. Peculiarities of the electronic responses are given in Sec. IVB. A discussion of electron-phonon coupling and intensity anomalies of the $B_{1g}$ phonon is found in Sec. IVB. Conclusions are drawn in Sec. VII.

II. EXPERIMENTAL DETAILS

A. Samples

We study $Y_{1-x}(Pr, Ca)_x Ba_2Cu_3O_{6+y}$ films with different doping levels achieved by substituting Y partially with Pr or Ca or by changing the chain-oxygen content y. Pr substitution and oxygen reduction allows us to reduce the doping while Ca substitution allows us to obtain higher dopings. We want to emphasize at this point that our Pr-123 films are reproducibly grown insulating antiferromagnets with well-defined two-magnon excitations. All films are grown by pulsed laser deposition on SrTiO$_3$(100) substrates and important properties are listed in Table II. While the substituted films are grown in a standard process, which is optimized to obtain high oxygen contents $y \approx 1$, we used reduced oxygen-partial pressures during cool down for the oxygen-reduced ones. Whereas the growth of the $Y_{1-x}Pr_xBa_2Cu_3O_{6+y}$ films has been optimized to obtain homogeneous and smooth films with low precipitate densities, the Ca-doped films exhibit somewhat poorer surface qualities, and a local variation of the Ca content from the nominal values cannot be excluded. However, also for these films the temperatures at which the superconductivity-induced features vanish are in good agreement with the transition temperatures. In the Pr- and the Ca-doped films a site-substitution disorder with respect to the Ba site cannot completely be ruled out. This disorder is promoted by the similar radii of the Ca, the Pr, and the Ba ions. Even in laser-deposited Y-123 films it has been shown that Y ↔ Ba site-substitution can occur. This disorder manifests itself via an increased c-axis parameter. Consequently, the phonon frequencies soften which can be used as an indication for the presence of disorder. Except for two films, which will be analyzed in Sec. IVB, all others are highly ordered exhibiting well-comparable properties and systematic doping dependencies.

All films in this study have high epitaxial qualities with large c-axis oriented fractions $\delta_c \geq 92 \%$ and high degrees of in-plane orientation $Q_{xy} \geq 92 \%$ determined by means of Raman spectroscopy as described elsewhere.
high quality is a prerequisite to study plane-polarized excitation geometries. In order to avoid surface contamination and oxygen depletion the films have been investigated shortly after preparation.

Given in Fig. 1 are the temperature dependencies of the resistivities of the films. Except for the film #Ca2 we observe decreasing resistivities with increasing doping as expected. The resistivities are slightly higher than those of single crystals [for Y-123 single crystals ρ(100K) = 50 μΩcm is a typical value]. The increased values may indicating additional sources of quasi-particle scattering. However, the temperature dependencies, i.e. the slopes of the resistivity curves, are remarkably similar to single crystal data. At high temperatures all films exhibit linearly decreasing resistivities. Deviations appear at lower temperatures, especially, in the underdoped films. This will be used to determine the pseudogap temperatures of the films in Sec. VIA. The transition temperatures, defined by zero resistance, range from $T_c = 56$ K in the underdoped film #Ox1 up to $T_c = 89.8$ K in the almost optimally doped film #Ox3 and back down to $T_c = 82.7$ K in the overdoped film #Ca2. The transition widths lie between $\Delta T_c \leq 10$ K at low and $\Delta T_c \leq 2$ K at high dopings.

The YBa$_2$Cu$_3$O$_{6+y}$ single crystal that has been investigated in this study has been grown in a zirconia crucible by a flux method described elsewhere. Prior to its investigation the surface has been etched in 1 % bromine in methanol in order to remove possible contaminants. Subsequently, the crystal was heated for several hours under 1 bar oxygen-partial pressure in order to ensure a maximum oxygen content close to $y=1$. According to its oxygen content a $T_c$ of $90 \pm 1$ K is expected for this crystal.

### B. Setup

For the Raman and transport investigations of the thin films they were mounted on the cold finger of a closed-cycle cryostat. The electrical measurements are performed in van-der Pauw geometry using lock-in techniques in the same setup. The crystal was mounted on the cold finger of a liquid He cryostat. For excitation the Ar$^+$ laser lines at 458 nm and 514 nm were used in the studies of the thin films and the single crystal, respectively. The thin film and single crystal studies have been performed in different setups described elsewhere with the spectral resolutions (HWHM) set to 3 cm$^{-1}$ and 2 cm$^{-1}$, respectively. In the thin film study usage of the laser line, which was always recorded together with the Raman spectra, ensures a high relative frequency accuracy of $\approx 0.2$ cm$^{-1}$. All spectra have been corrected for the spectral response of spectrometer and detector.

Spectra of the films #Ox1 and #Ox4 are additionally corrected in order to remove substrate signals. They appeared due the poorer ratio between the thickness (see Table 1) and the penetration depth (Ref. 87) in these films. In the thin film study we have used a power density of 110 W cm$^{-2}$ and an effective spot radius of 40 μm leading to a typical heating of 2 K in the laser spot at 100 K. The crystal has been investigated with power densities of 120 W cm$^{-2}$ and 270 W cm$^{-2}$ and an effective spot radius of 20 μm leading to typical heating of 4 K and 9 K in the laser spot at 100 K, respectively. All given temperatures are spot temperatures. B$_{1g}$ and B$_{2g}$ spectra are taken in polarization geometries which are denoted $z(x'y')$ and $z(xy)$ in Porto notation. Primed letters point out that the direction of polarization and the crystal axes of the substrate to describe the polarization geometries. In case of the single crystal no $z(xy)$ spectra have been taken.

### III. ANALYSIS OF RAMAN SPECTRA

#### A. Model

Apart from phonons, Raman spectra of cuprate superconductors consist of electronic (intraband) and magnetic (two-magnon) excitations. The latter dominate in the antiferromagnetic regime while the former gain spectral weight at higher dopings. When a phonon, characterized by its bare phonon frequency $\omega_p$ and its bare phonon linewidth $\Gamma$ (HWHM), couples to intraband excitations, described by an electronic response function $\chi^e(\omega) = R^e(\omega) + i\sigma^e(\omega)$, its line shape becomes asymmetric and its self-energy is renormalized. In case of the B$_{1g}$ phonon in Re-123 compounds simultaneous descriptions which consider the interacting background have been obtained in a microscopic approach by Devereaux et al. and a phenomenological one by Chen et al. We have shown recently that both approaches resemble each other to a large extent and have obtained the following expression for the imaginary part of the Raman response function $\text{Im}\chi_\sigma(\omega)$ which is accessible in Raman experiments in $\sigma$ symmetry:

$$\text{Im}\chi_\sigma(\omega) = \gamma_\sigma \delta_\sigma^\text{pp}(\omega) + \frac{\gamma_\sigma \delta_\sigma^\text{pp}}{\gamma(\omega)[1+\epsilon^2(\omega)]} \times$$

\[
\left\{ [R_\sigma^p(\omega) + R_{pp}]^2 - 2\epsilon(\omega)[R_\sigma^p(\omega) + R_{pp}] \delta_\sigma^\text{pp}(\omega) - \delta_\sigma^\text{pp}(\omega)^2 \right\},
\]

with the renormalized phonon parameters $\gamma(\omega) = \Gamma + \delta_\sigma^\text{pp}(\omega)$ and $\epsilon(\omega) = [\omega^2 - \omega_p^2(\omega)]/[2\omega_p \gamma(\omega)]$ with $\omega_p(\omega) = \omega_p^2 - 2\omega_p \delta_\sigma^\text{pp} R_\sigma^p(\omega)$. In the above expression...
\(\gamma_{\sigma}\) represents the symmetry elements of the electron-photon vertex projected out by the incoming and outgoing polarization vectors, \(g_{\sigma}\) is the lowest order expansion coefficient of the electron-photon vertex describing the coupling to non-resonant intraband electronic excitations which is independent of momentum but may vary with temperature, and \(R_{pp} = g_{pp}/(\gamma_{\sigma} \cdot g_{\sigma})\) with \(g_{pp}\) a constant representing an abbreviated “photon-phonon” vertex which describes the coupling to resonant interband electronic excitations. In the following we will refer to \(g_{\sigma}\) as the effective electron-phonon coupling constant. The measured Raman intensity \(I_{\sigma}(\omega)\) is related to the imaginary part of the electronic response function via the fluctuation-dissipation theorem:

\[
I_{\sigma}(\omega) = |1 + n(\omega)| I_{0,\sigma}(\omega) = A |1 + n(\omega)| \text{Im} \chi_{\sigma}(\omega), \quad (2)
\]

with \(n(\omega)\) the Bose factor, \(I_{0,\sigma}(\omega)\) the Raman efficiency, and \(A\) a proportionality constant. In order to arrive at a formula that allows us to model the Raman spectra we make the assumption that the phonon is only renormalized by the Raman-active electronic response \(\gamma_{\sigma}^{2} \chi_{\sigma}(\omega)\), neglecting all other self-energy contributions like, e.g., those due to anharmonic phonon-phonon interactions which are therefore included in \(\omega_{p}\) and \(\Gamma\). This assumption allows us to express the Raman efficiency in the following way:

\[
I_{0,\sigma}(\omega) = g_{\ast}(\omega) + \frac{C}{\gamma(\omega)[1 + \epsilon^{2}(\omega)]} \quad (3)
\]

\[
\times \left\{ \left[ \frac{R_{\text{tot}}(\omega)}{C} \right]^{2} - 2\epsilon(\omega) \frac{R_{\text{tot}}(\omega) g_{\ast}(\omega)}{C} - \left[ \frac{g_{\ast}(\omega)}{C} \right]^{2} \right\},
\]

with the constant \(C = \frac{A^{2}}{g_{\sigma}^{2}/\gamma_{p}^{2}}\) and the substitutions \(g_{\ast}(\omega) = C g_{\sigma}^{2} g_{\ast}(\omega)\) and \(R_{\text{tot}}(\omega) = R_{\ast}(\omega) + R_{0}\) with \(R_{\ast}(\omega) = C g_{\sigma}^{2} R_{\ast}(\omega)\) and \(R_{0} = C g_{\sigma}^{2} R_{pp}\).

Equation (3) can be simplified to resemble the conventional Fano formula:

\[
I_{\text{Fano}}(\omega) = C_{\text{Fano}} \frac{q + \epsilon_{\text{Fano}}(\omega)^{2}}{[1 + \epsilon_{\text{Fano}}(\omega)]^{2}} \quad (4)
\]

by setting \(\epsilon_{\text{Fano}}(\omega) = (\omega^{2} - \omega_{p}^{2})/(\omega_{p} \gamma_{p}) \simeq (\omega - \omega_{p})/\gamma_{p}\), the asymmetry parameter \(q = -R_{\text{tot}}(\omega_{p})/g_{\ast}(\omega_{p})\), and the intensity \(C_{\text{Fano}} = g_{\sigma}^{2}(\omega_{p})/(C \gamma_{p})\), where \(\omega_{p} = \omega_{p}(\omega_{p})\) and \(\gamma_{p} = \gamma(\omega_{p})\). In reference to the conventional Fano mechanism\(^{2}\) we find for the total and the bare phonon intensity \(I_{\text{tot}} = \frac{2}{\pi} R_{\text{tot}}^{2} (\omega_{p})\) and \(I_{\text{phon}} = \frac{2}{\pi} R_{0}^{2} = \pi A g_{\sigma}^{2}\).

With the above description of a Fano-type line shape measure of the electron-phonon coupling can be obtained in two independent ways. First, in relevant units, via the mass-enhancement factor \(\lambda\) defined by \(\lambda = 2 R_{\ast}(\omega_{p})/C = 2 g_{\sigma}^{2} R_{\ast}(\omega_{p})\). And second, in arbitrary units, via the reciprocal fit parameter \(1/C = g_{\sigma}^{2}/(A \gamma_{p}^{2})\).

For brevity we will drop the suffix \(\sigma\) in the discussion of the electron-phonon coupling in the following as we are only dealing with the Fano-type line shape of the \(B_{1g}\) phonon in \(B_{1g}\) symmetry in this work.

So far, a phonon is described by the four parameters \(\omega_{p}, \Gamma, R_{0},\) and \(C\). In addition, the frequency dependent real and imaginary parts of the electronic response have to be known. An expression that successfully models the imaginary and the real parts of electronic response function observed in cuprate superconductors is\(^{3}\)

\[
g_{\ast}(\omega) = I_{\infty} \tanh(\omega/\omega_{T}) + \left[ \frac{C_{2\Delta}}{1 + \epsilon_{2\Delta}^{2}(\omega)} - (\omega \rightarrow -\omega) \right] - \left[ \frac{C_{\text{sup}}}{1 + \epsilon_{\text{sup}}^{2}(\omega)} - (\omega \rightarrow -\omega) \right], \quad (5)
\]

where \(I_{\infty}, C_{2\Delta},\) and \(C_{\text{sup}}\) are fit parameters for the respective intensities, \(\omega_{T}\) and \(\omega_{2\Delta}\) are fit parameters for the crossover frequency of the background and the position of the 2\(\Delta\) peak, and \(\Gamma_{2\Delta}\) is the width (HWHM) of the 2\(\Delta\) peak. For the Lorentzians the abbreviations \(\epsilon_{2\Delta}(\omega) = (\omega - \omega_{2\Delta})/\Gamma_{2\Delta}\) and \(\epsilon_{\text{sup}}(\omega) = (\omega - \omega_{\text{sup}})/\Gamma_{\text{sup}}\) are used. While the first models the 2\(\Delta\) peak the second describes the suppression of spectral weight observed for \(\omega \rightarrow 0\). The second terms in the brackets are necessary to fulfill the symmetry requirements for the Raman response. The Lorentzian modelling the suppression is bound to the 2\(\Delta\) peak by setting \(2\omega_{\text{sup}} = 2\Gamma_{\text{sup}} = \omega_{2\Delta} - \Gamma_{2\Delta}\) in order to reduce the number of free parameters. The hyperbolic tangent which is used to reproduce the flat incoherent response is arbitrarily cut off at \(\omega_{\text{cut}} = 8000\) cm\(^{-1}\). As a consequence, the Hilbert transformed incoherent part contains a constant error.\(^{2}\) Due to this error the bare phonon frequency \(\omega_{p}\) and the resonant intensity contribution \(R_{0}\) cannot be determined accurately and depend on the chosen value of \(\omega_{\text{cut}}\). In detail, it turns out that \(R_{\ast}(\omega_{p})/C\) \{\(R_{0}/C\)\} increases \{decreases\} by \(I_{0}/C \cdot \frac{2}{\pi} \ln(\omega_{\text{cut}}/\omega_{\text{cut}}}\) when the cut-off frequency is varied. With a typical value of \(I_{0}/C = 1\) at optimal doping corrections of \(\sim 0.2\) cm\(^{-1}\) appear when \(\omega_{\text{cut}}\) is increased from 8000 cm\(^{-1}\) to 11000 cm\(^{-1}\). Whereas the absolute values of the bare phonon frequency and the bare phonon intensity have to be considered with some care for the reason given above, the relative changes at different temperatures are not affected.

Equations (3) and (4) allow us to describe a phonon together with the interacting background that renormalizes it. If several phonons are observed, each acquires an interference term as the one given in Eq. (3). An illustration of the fit parameters is shown in Fig. 3 where an artificial spectrum with a phonon superimposed is displayed. In the left panel the efficiency \(I_{0}(\omega)\), the interacting, and the non-interacting phonon contributions are shown. In the right panel the imaginary part of the electronic response function \(g_{\ast}(\omega)\) that is used in the description of the interacting phonon contribution and the separate background fractions are depicted. Instead of the fit parameter \(\omega_{2\Delta}\) we will use the center frequency of the peak in the imaginary part of the electronic response function.
function as a measure of the $2\Delta$ peaks in the respective symmetries. For simplicity we will refer to the imaginary part of the electronic response function in the following as the electronic response.

**B. Example**

To give an example we show in Fig. 3 the efficiencies $I_0(\omega)$ of the film #Ox4 in A$_{1g}$, B$_{1g}$, and B$_{2g}$ symmetry, measured well above and below the transition. We have normalized the B$_{1g}$ efficiency of the film #Ox4 at 18 K to unity above 650 cm$^{-1}$. After consideration of the laser power and the scan time, we use the same scaling factor for the spectra of all other films, geometries, and temperatures. No further manipulations are needed to obtain well-comparable spectra. In the order of their energy we observe in Fig. 3 the Ba mode at 120 cm$^{-1}$, the Cu(2) mode at 150 cm$^{-1}$, the B$_{1g}$ phonon which is the out-of-phase plane oxygen mode O(2)−O(3) at 340 cm$^{-1}$, the in-phase plane oxygen mode O(2)+O(3) at 430 cm$^{-1}$, and the apical oxygen mode O(4) at 500 cm$^{-1}$. These are the 5 Raman-active A$_g$ phonons of Y-123. Please note, that the appearance of the Ba and the O(4) mode in B$_{1g}$ symmetry is not related to the presence of a-axis oriented grains, as these modes also appear in single-crystal data with equal strength. Only in perfect tetragonal samples the phonons have exclusively A$_{1g}$ or B$_{1g}$ character. In the orthorhombic phase, i.e. at higher dopings, no exact selection rules apply and A$_{1g}$ modes can appear in B$_{1g}$ symmetry and vice versa. In addition to the allowed modes we always observe a weak feature around 590 cm$^{-1}$. This feature grows in the oxygen-reduced samples in which it is accompanied by other modes at 230 cm$^{-1}$ and 280 cm$^{-1}$. The modes at 230, 280, and 590 cm$^{-1}$ are modes of Y-123-O$_{6+\delta}$ dominated by vibrations of Cu(1) and O(1). They become Raman-active for $0 < \delta < 1$ due to disorder in the occupancy of the chain-oxygen site. As the 590 cm$^{-1}$ mode is also observed in fully oxygenated samples it is likely to assume that it also indicates other types of disorder, probably at the Ba site.

Whereas the Raman efficiencies in B$_{2g}$ symmetry are not altered by the superconducting transition in the film #Ox4, as seen in Fig. 3, two main features are observed in the other symmetries. Namely, an increasing background in A$_{1g}$ symmetry around 300 cm$^{-1}$ and an increasing B$_{1g}$ phonon intensity accompanied by a reduction of spectral weight below 250 cm$^{-1}$ in B$_{1g}$ symmetry. In order to identify the background features and to separate the phononic contribution the following description is used: (i) We describe the background with the expression given in Eq. 3. (ii) We describe strong Fano profiles, such as the B$_{1g}$ phonon in B$_{1g}$ (symmetry), and the Ba and the O(4) mode in A$_{1g}$, with the interference term of Eq. 4. (iii) We describe weak Fano profiles, such as the Ba mode in B$_{1g}$, and the B$_{1g}$ phonon in A$_{1g}$, with Eq. 4. (iv) We describe symmetric phonons, such as the Cu(2) mode in A$_{1g}$, with Lorentzians.

The A$_{1g}$ efficiency of the film #Ox4 at 18 K and its description are given in the uppermost spectrum of Fig. 4(a). Below, the modeled phononic signal is displayed, i.e. the Lorentzians and the simple and improved Fano profiles. Above $\sim 120$ cm$^{-1}$ the phononic signal becomes negative as a consequence of the destructive interference of Ba mode and background. Subtracting the phononic signal from the efficiency we obtain the electronic back-ground $g_0(\omega)$ which is shown in the second spectrum from the bottom. In the background a $2\Delta$ peak at $\sim 280$ cm$^{-1}$ as well as a monotonically decreasing intensity for $\omega \to 0$ can be identified. At the bottom of Fig. 4(a) the real part of the electronic background $R_\epsilon(\omega)$ is shown. In order to obtain $R_\epsilon(\omega)$ we have performed a numerical Hilbert transformation of $g_0(\omega)$. For the transformation the measured spectrum is taken as constant for high frequencies up to $\omega_{cut}$ and is interpolated to zero intensity at $\omega = 0$; for negative frequencies the antisymmetry of $g_0(\omega)$ has been used. Evidently, the description of $R_\epsilon(\omega)$ used in the fit agrees well with the numerically obtained data.

Similarly to Fig. 4(a) we show in Fig. 4(b) the results of the analysis of the B$_{1g}$ efficiency of the film #Ox4 at 18 K. Due to the strong coupling of the B$_{1g}$ phonon to the electronic background, as evidenced by the high asymmetry of the profile, there is a substantial “negative intensity” observable in the phononic signal right at the position of the $2\Delta$ peak. This explains why the $2\Delta$ peak in B$_{1g}$ symmetry is hardly seen in the raw data shown in Fig. 3. In fact, a simple division of spectra in order to obtain a measure of the $2\Delta$ peak yields misleading results when strong Fano profiles are present. The features seen in the electronic background in B$_{1g}$ symmetry are a $2\Delta$ peak at $\sim 390$ cm$^{-1}$, i.e. higher than in A$_{1g}$ symmetry, and a decreasing background at small Raman shifts which falls off with $\sim \omega^{-4}$ from the peak down to 270 cm$^{-1}$ and with $\sim \omega^{1.0}$ at lower frequencies.

In Fig. 5 we present the temperature evolution of the backgrounds in A$_{1g}$ and B$_{1g}$ symmetry which have been obtained after subtraction of the phononic signals from the efficiencies as explained above. One can still identify the positions of the strongest phonons via the increased noise levels which grow as $\sqrt{I_0(\omega)}$. In addition, a typical renormalized frequency of the B$_{1g}$ phonon is indicated via a dashed-dotted line in the right panel. At the bottom the 18 K data are shown. With increasing temperature we observe that the $2\Delta$ peaks broaden while they consecutively shift to somewhat lower energies. Above 57 K the background features have vanished in A$_{1g}$ symmetry while a weak bump around 300 cm$^{-1}$ remains up to 87 K in B$_{1g}$ geometry. In this geometry, the background feature passes the B$_{1g}$ phonon between 57 K and 77 K. Above 87 K a completely flat background is observed above 200 cm$^{-1}$ in both geometries. These backgrounds are almost entirely described by the incoherent contribution, expressed via the first term in Eq. 4, except for small broad humps at the positions where the $2\Delta$ peaks
are observed close to $T_c$ which are hardly resolvable in Fig. 3.

IV. OXYGEN DOPING

The simplest way to vary the doping in the cuprate superconductors is by changing their oxygen content. Under useful conditions it is possible to vary only the oxygen content in the charge-reservoir layers where the binding energies are typically weaker than in the CuO$_2$ planes. In principle, this can be done during the preparation choosing specific oxygen-partial pressures. Often the oxygen content is changed ex-situ, e.g. after single crystals have been separated from the melt. In the RE-123 system the charge reservoir is provided by the copper-oxygen chains. During the laser deposition the Y$_{1-x}$(Pr,Ca)$_x$Ba$_2$Cu$_3$O$_{6+y}$ films are tetragonal with $y \approx 0$. High oxygen contents of $y \approx 1$ are achieved during cool down in 1 bar oxygen. In order to obtain the oxygen-reduced films this pressure has been decreased to values which are given in Table 1.

A. Thin Films

In Fig. 3 we show the electronic responses $\rho_e(\omega)$ of the oxygen-doped films in A$_{1g}$ and B$_{1g}$ symmetry obtained after subtracting the phononic excitations from the efficiencies. As substantial substrate signal was present in the $z(x'x')\pi$ spectra of the film #Ox1 this background will not be discussed. Similar to Fig. 3 we find increased noise levels at the positions of the strongest phonons in Fig. 3. In agreement with previous studies on single crystals of Y-123 (Ref. 29) and of Bi-2212 (Ref. 31) we find increasing energies and decreasing intensities of the 2∆ peaks in B$_{1g}$ symmetry with decreasing doping. At the lowest doping in the film #Ox1 ($y \approx 0.52$) the 2∆ peak has vanished. This was also observed in single crystals, where studies in A$_{1g}$ symmetry revealed a vanishing 2∆ peak as well. However, the 2∆ peaks do not vanish equally fast in A$_{1g}$ symmetry and comparable strengths are observed for the films #Ox2, #Ox3, and #Ox4. Another difference to the B$_{1g}$ feature is that the A$_{1g}$ 2∆ peak follows $T_c$ having a a maximum value in the almost optimally doped film #Ox3 with $\sim 305$ cm$^{-1}$. Regarding the power laws we find different behaviors in A$_{1g}$ and B$_{1g}$ symmetry. Whereas the A$_{1g}$ response below $\sim 250$ is proportional to $\omega^{1.0}$ in all films, the B$_{1g}$ responses for $\omega \rightarrow 0$ changes slope with exponents of 1.00, 0.90, 0.4, and 0.2 in the films #Ox4, #Ox3, #Ox2, and #Ox1, respectively. Whereas the gap features are strongly doping dependent in B$_{1g}$ symmetry, the responses above 650 cm$^{-1}$ exhibit comparable intensities. Similarly, we find that the A$_{1g}$ responses are well-comparable above 650 cm$^{-1}$.

The temperature dependencies of the fit parameters of the B$_{1g}$ phonons are shown in Fig. 7 in which the doping increases from left to right. Beside the bare phonon parameters and the self-energy contributions at $\omega = \omega_p$ also the renormalized frequencies $\omega_p$ and linewidths $\gamma_p$ are depicted which facilitates a comparison with previous data obtained with the simple Fano description according to Eq. (4). Solid lines are fits to the anharmonic decay for both models and anomalies below $T_c$ are discussed with respect to these fits. Looking at the renormalized phonon parameters we observe softenings in the films #Ox2, #Ox3, and #Ox4 in agreement with the relative positions of the B$_{1g}$ 2∆ peaks and the phonon energies. No superconductivity-induced change is observed in the film #Ox1 in which the 2∆ peak is absent. In the film #Ox4, which exhibits a B$_{1g}$ 2∆ peak in the vicinity of the phonon we find a strong broadening of 5.3 cm$^{-1}$. In contrast, slight sharpenings of 0.5 cm$^{-1}$ and 0.8 cm$^{-1}$ are observed in the films #Ox3 and #Ox2, in which the B$_{1g}$ 2∆ peaks evolve at substantially higher energies.

Our fit procedure now allows us to identify the self-energy effects which originate from the backgroup. As we have already observed in a previous study we find a convincing correlation between the changes of the linewidth appearing below $T_c$ and the varying self-energy contributions $\rho_e(\omega_p)/C$ for the B$_{1g}$ phonon in RE-123 films. It turns out that the slight sharpenings in the films #Ox2 and #Ox3 are a consequence of reduced effective couplings at low temperatures, as the background intensities at the phonon position $\rho_e(\omega_p)$ are hardly affected. The broadening in the film #Ox4, however, is almost entirely described by a slightly increased intensity $\rho_e(\omega_p)$ accompanied by a substantially increased effective coupling.

There are two different representations of the effective electron-phonon coupling in Fig. 7. First, we show the real part of the self-energy $R_e(\omega_p)/C$ which is proportional to the mass-enhancement factor $\lambda$ with $\lambda = 2R_e(\omega_p)/(C \cdot \omega_p) = 2g^2 \frac{R^2}{\omega_p}$. Second, we display $I_\infty/C = g^2 \frac{R^2}{\omega_p}$ which is the inverse fit parameter $C$ normalized by the background intensity measured at high Raman shifts $I_\infty$. While $\lambda$ allows us to quantify the strength of the coupling in relevant units, $I_\infty/C$ is a more accurate measure, however, only in arbitrary units. It can be seen in Fig. 7 that both representations of the effective coupling closely follow each other and increase with increasing doping. In detail, we obtain almost vanishing coupling in the film #Ox1 with $\lambda \rightarrow 0.004$ for low temperatures whereas $\lambda \approx 0.015$ in the films #Ox2, #Ox3, and #Ox4 above $T_c$. As already mentioned, somewhat decreasing couplings are observed in the films #Ox2 and #Ox3 below $T_c$. In contrast, we find a remarkable strengthening of the coupling in the film #Ox4 at low temperatures.

We now turn to the lowest panel in Fig. 7 in which besides the total intensities $I_{\text{tot}}$ also the bare phonon intensities $I_{\text{phon}}$ are given. Even though increasing intensities $I_{\text{tot}}$ are observed below $T_c$ in all films, they have different...
origins. Whereas the increase in the film #Ox4 is a result of an increasing background contribution \( R_s(\omega_p) \) accompanied by an increasing effective coupling, the increase in the other films originate from increasing values of \( R_0 \) which compensate the decreasing effective couplings. In detail, it turns out that the bare phonon intensity \( I_{\text{phon}} \) shows a change of slope at low dopings and a minimum in the film #Ox4 at temperatures which increase monotonically with decreasing doping. It appears as if the effective coupling approaches a maximum value close to this temperature. Moreover, we find that the onsets of the softening in \( \omega_p \) and \( \omega_\nu \) are correlated with this temperature which is e.g. more than 10 K above \( T_c \) in the film #Ox2.

B. Single Crystals

A similar study of the doping dependence of the background features and of the phonon self-energy effects has been carried out by Irwin and co-workers who have investigated Y-123 single crystals with different oxygen contents grown by Liang et al. While Altendorf et al. focused on the \( B_{1g} \) phonon over a wide doping range down to \( \lambda \approx 0.7 \) using the simple Fano formula given in Eq. \( 8 \) Chen et al. explored the \( 2\Delta \) peaks for \( 0.93 \leq \lambda \leq 1 \) using an expression similar to Eq. \( 8 \). In the work of Chen et al. a Green’s function model based on the approaches of Nitzan et al. and Klein et al. is used in order to obtain a simultaneous description of the phononic and electronic excitations. Being mainly interested in the electronic background, Chen et al. considered an electronic response function with a frequency dependent imaginary and a constant real part. Especially, they assumed that the real part is small. Comparison with Fig. 8 shows, that \( R_{\text{el}}(\omega) \) will only be constant for a sufficient energy range when \( \omega_\nu > (2\Delta + \Gamma_{2x}) \) or \( \omega_\nu < (2\Delta - \Gamma_{2x}) \). Also, we find that \( R_{\text{el}}(\omega) \) is of the order of or even exceeds \( g_\nu(\omega) \) in contrast to the above assumption. The backgrounds obtained in their study must therefore not be identical to the ones that would have been obtained using Eqs. \( 8 \) and \( 9 \).

In order to facilitate a comparison of our results with the previous works but also in order to identify possible differences between the behaviors of single crystals and thin films we have investigated a single crystal also grown by Liang et al. Spectra and backgrounds of the single crystal are shown in Fig. 8. Here, efficiencies containing \( A_{1g} + B_{2g} \) symmetry are shown, as we did not take measurements in \((xz)\) geometry. However, as the \( B_{2g} \) response is small comparison to the one in \( A_{1g} \) symmetry and as the superconductivity-induced changes are weaker (see Fig. 3), the spectra are dominated by the \( A_{1g} \) response which facilitates a comparison with the thin film data. In order to make this comparison easier, we normalize the intensities such that the \( B_{1g} \) efficiency above 700 cm\(^{-1}\) approaches unity in the 18 K spectrum and use the same factor for the other temperatures and the other geometry as well. With this scaling factor it turns out that the intensity of the \( B_{1g} \) phonon is comparable to the intensities seen in the films at least in the normal state (see Fig. 8). However, due to the better spectral resolution and also because the natural linewidth in long-range ordered single crystals is smaller than in the films, the \( B_{1g} \) phonon peak height to background ratio is stronger in Fig. 8(a) than the one seen in Fig. 8. As the single crystals have large unwinned domains, enhanced orthorhombic distortions are present and the Cu(2) and the O(2)+O(3) modes appear in \( B_{1g} \) efficiency in addition to the Ba and the O(4) mode. For the same reason a relatively strong \( B_{1g} \) phonon is observed in \( A_{1g} + B_{2g} \) symmetry. Similar observations have been made by Chen et al.

Regarding the electronic backgrounds of the single crystal in \( A_{1g} + B_{2g} \) and \( B_{1g} \) symmetry, which are shown in Fig. 8(b), we find small features than in the films: A strong \( 2\Delta \) peak in \( A_{1g} + B_{2g} \) symmetry with a linear slope of \( \sim \omega^{1.1} \) at small Raman shifts and a weaker \( 2\Delta \) peak in \( B_{1g} \) symmetry which falls down from the peak with a power of \( \sim \omega^{3.0} \) and has a reduced slope of \( \sim \omega^{1.0} \) below 270 cm\(^{-1}\). The intensities of the \( 2\Delta \) peaks in the crystal are distinctly stronger than those of the films. Also, the energies of the \( 2\Delta \) peaks differ from those in the films with a \( 2\Delta \) peak of \( \sim 335 \) cm\(^{-1}\) in \( A_{1g} + B_{2g} \) symmetry and a \( B_{1g} \) \( 2\Delta \) peak of \( \sim 435 \) cm\(^{-1}\). Both values are higher than those observed in the Y-123 film #Ox4 indicating a lower doping level. Again one can see that the strong anti-resonance inhibits a clear identification of the \( B_{1g} \) \( 2\Delta \) peak in the raw data of Fig. 8(b).

The self-energy effects of the \( B_{1g} \) phonon of the single crystal are given together with those of the oxygen-doped films in Fig. 8. Due to the better signal to noise ratio and the better spectral resolution we used smaller symbols to indicate the smaller error bars. The absolute values of the frequencies and linewidths differ somewhat from those observed in the films. Smaller linewidth appear as a consequence of the higher spectral resolution used in this study. In addition, they reflect the increased grain size, i.e. the long-range order, of the single crystal. Increased frequencies are most likely related to the smaller \( c \)-axis parameter of fully oxygenated single crystal compared to those of fully oxygenated thin films. Even though the absolute frequencies and linewidths do not agree, the self-energy effects, the effective coupling, and the intensities are well-comparable.

Looking at the phonon-self energy effects depicted in Fig. 8 it turns out that the bare phonon follows the expected anharmonic decay to a large extend. Only a small increase of the bare phonon linewidth exists close to \( T_c \), whereas a significant softening of \( \omega_\nu \) appears at low temperatures. While the strengths of the coupling in the crystal agrees with that of the film #Ox4 at very high and low temperatures, the coupling in the crystal starts to increase already below 250 K exceeding the film value at \( T_c \) by almost a factor of two with \( \lambda \approx 0.023 \). The bet-
ter signal to noise ratio allows us to identify clearly an intermediate maximum of the coupling appearing slightly below $T_c$ very clearly. This maximum appears right at that temperature at which a small intermediate broadening in the renormalized phonon linewidth is observed and the bare phonon starts to soften. Moreover, a distinct minimum of the bare phonon intensity $I_{\text{phon}}$, similar to the one seen in the film #Ox4, appears in the same temperature regime. The temperature at which the anomalies occur is higher than in the film #Ox4 which is another indication of a lower doping in the single crystal in view of the doping dependence of this temperature in the oxygen-doped films. At low temperatures the total intensity is significantly stronger than those of the films. This is related to the strong intensity of the $B_{1g}$ $2\Delta$ peak in the single crystal.

V. ELEMENT SUBSTITUTIONS

Many cuprate superconductors offer the possibility to vary the doping via the exchange of ions with different valences. Well-known exchange pairs are Sr$^{2+}$ ↔ La$^{3+}$, e.g. in the La-214 compounds, or Y$^{3+}$ ↔ Ca$^{2+}$, e.g. in the Bi-2212 compounds. The first allows one to dope holes while the second reduces the hole concentration. Often this approach is limited as some materials become unstable when the dopant concentration exceeds a certain value. Stable Ca-substituted Y-123 compounds are obtained up to a dopant concentration of 0.5. However, in these samples Ca also substituted the Ba site, and the relative fraction of Ca on the Y site dropped with increasing Ca content. For $x \leq 0.2$ less than 20 % of the Ca substituted the Ba site. $Y_{1-x}\text{Pr}_x$-123 is a stable compound for all Pr concentrations up to pure Pr-123. The reason why Pr substitution is varying the doping when replacing a rare-earth atom in a RE-123 compound is generally attributed to its capability to localize holes in hybridized orbitals of Pr $4f$ and adjacent O $2p$. However, recently it has been suggested that substantial site-substitution disorder with respect to a Pr ↔ Ba exchange is inhibiting superconductivity in Pr-123. In fact, the latter authors claimed to find superconductivity in samples in which Pr is exclusively occupying the rare-earth site. Recently, however, it was argued that the small magnetic moments observed in the superconducting Pr-123 samples rather indicates that Pr is present at the Ba-site in a substantial volume fraction. The high resistivity of the superconducting Pr-123 samples as well as the impossibility to prepare them with a high purity in large volume fractions, as was stated by the authors of Ref. 34 are further indications for the presence of strong site-substitution disorder in superconducting Pr-123.

As already stated above, our Pr-123 films are reproducibly grown insulating antiferromagnets. However, in these films as well as in the Ca-substituted ones a site-substitution disorder appearing at the Ba and the RE site cannot completely be ruled out, as the growth conditions during the laser deposition are away from equilibrium. The appearance of disorder can depend on the morphology of the substrate surface or on slight changes in the preparation conditions which cannot be controlled in all details. It manifests itself in decreased phonon frequencies and a weakened and broadened Ba phonon peak as noted in Sec. IV. In the following sections we will compare the Raman spectra of ordered and disordered films beginning with the former ones.

A. Ordered Samples

Figure 10 shows the electronic responses $\rho_s(\omega)$ of the ordered films #Pr2, #Pr3, and #Ca2 at 18 K in $A_{1g}$ and $B_{1g}$ symmetry. For comparison with the oxygen-doped films, the energies of the $2\Delta$ peaks of the film #Ox4 are given as dashed lines. In case of the film #Pr3 we did not measure the $B_{2g}$ spectra directly. However, as will be shown in Sec. VI C, the measured $B_{2g}$ responses of the under- or slightly overdoped films varied hardly. Therefore, we subtracted the $B_{2g}$ spectra of the film #Pr2 from the $z(x'y')\tau$ data of the film #Pr3 in order to obtain its $A_{1g}$ response. The strengths of the background features in these films are comparable to those in the oxygen-reduced films. Regarding the $B_{1g}$ responses in Fig. 7 we observe a similar behavior as in the oxygen-doped films: With decreasing doping the $2\Delta$ peak shifts to increasing frequencies from $\sim 305 \text{ cm}^{-1}$ in the film #Ca2 up to $\sim 580 \text{ cm}^{-1}$ in the film #Pr3. Concomitantly, we observe a change of slope at Raman shifts below 270 cm$^{-1}$ from $\sim \omega^{1.7}$ in the film #Ca2 to $\sim \omega^{0.4}$ in the film #Pr2. Note, that while the $T_c$'s of the films #Ca2 and #Pr3 vary by only 4 %, their $2\Delta$ peaks vary by almost a factor of two. Even though the $B_{1g}$ responses of the similarly low-doped samples #Pr2 and #Ox1 are flat, showing no indication of a $2\Delta$ peak, the Pr-doped sample has a 50 % stronger intensity at high Raman shifts. Another remarkable difference to the oxygen-doped samples appears, if we look at the $A_{1g}$ responses. Here, we observe a strong $2\Delta$ peak even in the low-doped sample #Pr2. At similar dopings the $A_{1g}$ $2\Delta$ peaks in oxygen-reduced samples have been observed to vanish. The energies of the $A_{1g}$ $2\Delta$ peak follow again the $T_c$'s of the samples showing a maximum value of $\sim 325 \text{ cm}^{-1}$ in the film #Pr3. Also, we find that the slopes at small Raman shifts are almost linear with $\sim \omega^{1.05\pm0.15}$ similar as in the oxygen-doped films. The $A_{1g}$ efficiencies at high Raman shifts, however, are significantly increased in the Pr-substituted films compared to the oxygen-doped ones. These efficiencies even exceed the values observed in Bi$_{12}$ symmetry.

The temperature dependencies of the self-energy effects of all substituted films are depicted in Fig. 11 where the doping level increases from left to right. Again the bare as well as the renormalized phonon parameters are given together with the self-energy contributions at
\[ \omega = \omega_p. \] Comparing the renormalized frequency of the ordered films with the expected values according to the anharmonic decays we observe softenings of 5 cm\(^{-1}\) and 1.5 cm\(^{-1}\) in the films \#Pr2 and \#Pr3, respectively, as well as a hardening of 1 cm\(^{-1}\) in the film \#Ca2. The frequency shifts are in agreement with the relative positions of the B\(_{1g}\) 2\(\Delta\) peaks and the phonon energies. When comparing the renormalized linewidths of the ordered films with the anharmonic decays we observe a broadening of 5.4 cm\(^{-1}\) in the film \#Ca2, in which the B\(_{1g}\) 2\(\Delta\) peak evolves in the vicinity of the phonon. The broadening is well-comparable to the one observed in the film \#Ox4. In the other films \#Pr2 and \#Pr3 we observe sharpenings of 2.5 cm\(^{-1}\) and 1.5 cm\(^{-1}\), respectively, which are clearly stronger than the softenings in the oxygen-reduced films. This holds especially for the film \#Pr2, as we did not observe any linewidth anomaly in the film with the lowest oxygen content \#Ox1.

We now relate the self-energy effects of the B\(_{1g}\) phonon in the ordered substituted films to the shape of and the coupling to the observed electronic responses. It turns out that neither the bare frequencies \(\omega_p\) nor the bare linewidth \(\Gamma\) follow the anharmonic decay in any of the ordered films. For instance, we find a sharpening of \(\Delta \Gamma = -2\) cm\(^{-1}\) in the film \#Pr2 and a broadening of \(\Delta \Gamma = 2\) cm\(^{-1}\) in the film \#Ca2 as well as concomitant softenings and hardenings of \(\Delta \omega_p = -2.5\) cm\(^{-1}\) and \(\Delta \omega_p = 4\) cm\(^{-1}\), respectively. As only weak or even vanishing B\(_{1g}\) 2\(\Delta\) peaks are observed in the Pr-doped samples (see Fig. 3) it is not surprising that the strong softenings and sharpenings which appear below \(T_c\) in these films cannot be attributed to the redistribution of the background. However, in the film \#Ca2 a strong B\(_{1g}\) 2\(\Delta\) peak was observed and the remaining discrepancies are unexpected.

The two representations of the coupling \(R_\omega(\omega_p)/C\) and \(I_\infty/C\) given in Fig. 3 are similarly good correlated as those in Fig. 2. Also, we find that the effective couplings, which are well-comparable to the values observed in the oxygen-doped films, weaken with decreasing doping. In the highest doped film \#Ca2 we observe an increasing effective coupling \(I_\infty/C\) below \(T_c\) similar as in the film \#Ox4, whereas decreasing effective couplings are observed in the other two films at low temperatures. While increasing bare phonon intensities \(I_{\text{phon}}\) are observed in the lowest row in the two Pr-doped films, a monotonic decrease is observed in the film \#Ca2 below \(T_c\). The latter is in agreement with a previous study of us [4] in which an increase of the total phonon intensity \(I_{\text{tot}}\) was absent in films whose 2\(\Delta\) peaks are below the phonon frequency for all temperatures. Similar as in the oxygen-doped films we find that the bare phonon intensity \(I_{\text{phon}}\) shows a change of slope at low dopings and a minimum in the film \#Ca2 at those temperatures where a strong effective coupling is observed. Moreover, an increase of this temperature with decreasing doping is observed in Fig. 10 as well.

### B. Disordered Samples

In order to study the influence of disorder on the Raman response and on the phonon self-energy effects we have chosen two pairs of films, one pair with a Pr content of 20\% and one pair with a Ca content of 5\%. The ordered films, which have been presented before, are \#Pr2 and \#Ca2, the disordered films are \#Pr1 and \#Ca1. The A\(_{1g}\) response of the film \#Pr1 was obtained by subtracting the B\(_{2g}\) spectra of the film \#Pr2 from its \(z(x'x')\) data similar as for the film \#Pr3. In Fig. 11 the backgrounds of the two pairs of films are shown. Clearly, the disordered films exhibit weaker background features in A\(_{1g}\) as well as in B\(_{1g}\) symmetry. In addition, we observe shifts of the 2\(\Delta\) peaks. It turns out, that the A\(_{1g}\) and B\(_{1g}\) 2\(\Delta\) peaks in the film \#Ca1 appear at \(\sim 270\) cm\(^{-1}\) and \(\sim 350\) cm\(^{-1}\), respectively, corresponding to increases of 25 cm\(^{-1}\) and 45 cm\(^{-1}\) in comparison to the film \#Ca2. The A\(_{1g}\) 2\(\Delta\) peak of the film \#Pr1, however, has a lower energy of \(\sim 270\) cm\(^{-1}\) compared to \(\sim 290\) cm\(^{-1}\) in the film \#Pr2. Independent of the disorder we observe that A\(_{1g}\) and B\(_{1g}\) responses merge above the 2\(\Delta\) peaks in the Ca-doped films whereas they are offset by some constant value in the Pr-doped ones.

We now come to the self-energy effects of the disordered films which are depicted in Fig. 10 in shaded columns. Regarding the renormalized frequencies we find a softening in the film \#Ca1 whereas a hardening was observed in the film \#Ca2. This correlates well with the position of the B\(_{1g}\) 2\(\Delta\) peak which exceeds the phonon frequency in the film \#Ca1 in contrast to the film \#Ca2. Whereas a strong hardening of the bare phonon frequencies was observed in the film \#Ca2, it follows the anharmonic decay in the film \#Ca1. In agreement with the decreased intensity of the background feature seen in Fig. 10 the broadening in the disordered film \#Ca1 is weaker than in the ordered one. In a similar manner the sharpening in the film \#Pr1 is smaller than the one in the film \#Pr2. The softenings of the bare and the renormalized phonon frequencies are more pronounced in the disordered film \#Pr1 than in the ordered. Moreover, they appear at a remarkably high temperature of 150 K. However, all other phonon frequencies soften below this temperature as well (not shown). This indicates that the softening is rather a signature of a lattice instability occurring in this temperature range than a result of a particularly strong interaction with electronic excitations.

Comparing the strengths of the effective couplings between the disordered and the ordered film we find corresponding values with respect to both, \(R_\omega(\omega_p)/C\) and \(I_\infty/C\). Whereas the maximum effective coupling in the film \#Ca1 is observed for \(T \to 0\) similar as in the film \#Ca2, the maximum effective coupling in the Pr-doped disordered film is observed at somewhat higher temperatures near the temperature of the lattice instability. Another difference between disordered and or-
dered films is related to the bare and total intensities of the B1g phonon. Clearly, \( I_{\text{phon}} \) and \( I_{\text{tot}} \) are smaller in the film \#Ca1 than in the film \#Ca2 down to 100 K. Below that temperature a superconductivity-induced increase is observed in \( I_{\text{tot}} \) in the film \#Ca1. This finding is in agreement with our observations in the ordered films, in which increasing intensities at low temperatures have only been observed when the energy of the B1g 2\( \Delta \) peak for \( T \to 0 \) exceeds the phonon value. An intensity anomaly is also observed in the film \#Pr1, however, the ratio \( I_{\text{tot}}(18\text{K})/I_{\text{tot}}(152\text{K}) \) is 35 \% smaller than in the film \#Pr2.

VI. DISCUSSION

A. Doping Levels and Pseudogap Temperatures

The doping level \( p \) is defined as the number of holes per CuO_2 plane in the unit cell. In order to determine \( p \) for the \( YM_x\text{Pr}_{1-x}\text{Ca}_2\text{O}_{6+y} \) films two different methods are used. The first method relies on a general \( \rho(T) \) relation which was proven to be valid for various HTS compounds by Tallon et al.\(^{102} \)

\[
\rho_c(p) = \rho_{\text{c,max}}(1 - 82.6(p - 0.16)^2) .
\]

In our study we used a maximum transition temperature \( \rho_{\text{c,max}} = 90 \pm 1 \text{ K} \) for the thin films taken from a recent systematic study.\(^{102} \) The thus calculated doping values are given in Table I.

The second method uses the Pr, Ca, or oxygen contents and specific \( T_c(x) \) and \( T_c(y) \) relations. In case of the Ca-doped films the simple relation \( p = 0.187 + \frac{x}{2} \) has been given by Tallon et al.\(^{102} \) This relation relies on the fact that fully oxygenated Y-123 has a doping value of \( p = 0.187 \) which was estimated in the same work. For the Pr-doped films we use the above estimate for \( x = 0 \) and take into account that \( T_c \) vanishes for Pr contents \( x \approx 0.5 \) (Ref.\(^{103} \)) which corresponds to \( p \approx 0.05 \) according to Eq. (6). Consequently, we employ \( p = 0.187 - 0.274x \) for the Pr-doped films. The mean value of both methods \( p \) is used in the following except for the disordered films \#Pr1 and \#Ca1. For these two films we will only take into account the values calculated from the transition temperature as the disorder invalidates the other consideration. Comparing the two disorder-order-pairs \((\#\text{Ca1} / \#\text{Ca2}) \) and \((\#\text{Pr1} / \#\text{Pr2}) \) we find decreased doping levels in the disordered films.

To determine \( p \) for the oxygen-doped films, the relation \( p = -0.023 + 0.21y \), valid for \( 0.45 \leq y \leq 1 \), has been taken from Ref.\(^{102} \). Application of this formula requires knowledge of the oxygen contents which have been determined as follows: In case of the film \#Ox4 we can put \( y = 1 \) as this film has been prepared with a high oxygen-partial pressure during the cool down. For the other films we may use \( T_c(y) \) relations obtained from published data.\(^{102} \) With \( T_c = 56.0 \text{ K} \) we find \( y = 0.52 \pm 0.03 \) for the film \#Ox1. For the last two films an estimation of the oxygen content with the same method is not useful as their \( T_c \)’s are close to the optimal value of 90 K for our films. In order to estimate their oxygen contents we made use of the intensity of the disorder-induced Raman mode at 230 cm\(^{-1} \) which only appears when copper-oxygen chains are interrupted.\(^{104} \) The relative intensities of this mode at 290 K are 100 \%, 51 \%, and 23 \% for the films \#Ox1, \#Ox2, and \#Ox3, respectively (B1g spectra at 18 K are shown in Fig. 17). In the presence of long-range order one would expect the strongest intensity of this mode near \( y \approx 0.75 \), and a decreased intensity for \( y \approx 0.5 \) when only every second chain is filled in the ortho-II phase.\(^{105} \) However, as a result of the lattice mismatch to the substrate the investigated films here are heavily twinned inhibiting a long-range order of the chain oxygen. Assuming therefore randomly occupied chain-oxygen sites and considering only a central and two neighboring unit cells we have calculated the probability of interrupted chains as a function of the chain-oxygen content \( y \).\(^{105} \) In this calculation a maximum probability for an interrupted chain is found at \( y \approx 0.6 \). With the knowledge of the oxygen content of the film \#Ox1 we could estimate the oxygen contents and, as a result, the doping values of the films \#Ox2 and \#Ox3 which are given in Table I.\(^{106} \) Similar as in the Pr- and Ca-doped films we will use the mean value \( \bar{p} \) from the dopings determined via Eq. (6) and via the oxygen contents in the following.

As has been noted in Sec. II A, the resistivity curves given in Fig. 3 deviate from the linear behavior \( \rho(T) = \rho(0) + \alpha T \) below a certain temperature. Similar observations have been made in single crystal studies and the temperature at which the deviation occurs has been identified as the pseudogap temperature \( T^* \).\(^{106} \) In order to show the different \( T^* \) of the films it is advisable to use the representation of the resistivity shown in Fig. 12. Here, the resistivities are normalized by the slope \( \alpha \) of the \( T \)-linear part after \( \rho^\ast = 0 \) has been subtracted. We use a 1 \% criterion to determine \( T^\ast \) from these graphs, meaning that \( [\rho(T^\ast) - \rho(0)]/\alpha T^\ast \approx X - 0.01 \). Here, \( X \) is the saturation value of the normalized resistivity at low temperatures which is in the regime 1 \pm 0.005 in this study. The estimated pseudogap temperatures are given in Table I.\(^{106} \) We find that the ordered films exhibit increasing pseudogap temperatures with decreasing doping. The two disordered films \#Pr1 and \#Ca1 clearly differ from this behavior with \( T^\ast = 100 \pm 5 \text{ K} \) and \( T^\ast = 145 \pm 10 \text{ K} \), respectively. Additional scattering contributions or structural instabilities are two possibilities that could be responsible for the differences. In case of the film \#Ox1 we find deviations from the linear \( T \)-dependence of the resistivity almost in the entire temperature range studied. As this hinders an estimation of \( T^\ast \), its value is given in brackets in Table I.

At comparable dopings oxygen-reduced films have
significantly higher pseudogap temperatures than Pr-substituted ones. This could be related to a stronger c-axis coupling present in the Pr-doped films in which the copper-oxygen chains remain unaltered. It could also be related to the presence of the hole-localizing Pr atoms right between the planes which may act as strong scatterers and thereby hinder the formation of the pseudogap. In case of the oxygen-doped films a comparison with published single crystal data can be carried out. It shows that the $T^*$ of the films are higher than those of the crystals which are below 220 K for $y \geq 0.78$. This could again be related to a decreased c-axis coupling as a greater disorder in the occupation of the chain-oxygen site can be expected in the strongly twinned films. According to published results a pseudogap temperature of $\sim 370$ K would be expected at the oxygen content of the film #Ox1 which is in agreement with our failure to estimate one in this film.

**B. Phonon Self-Energies**

In the upper panel of Fig. 13 we have depicted the differences between the renormalized linewidths for $T \to 0$ and the values expected from the anharmonic decays of the investigated films and the single crystal versus energy of their $B_{1g} 2\Delta$ peaks. In the lower panel the corresponding graph for the renormalized frequencies is given. Beside the results of this study also single crystal data obtained by Altdorf et al. are included. The corresponding $B_{1g} 2\Delta$ peaks are taken from the work of Chen et al. who investigated the same crystals. Together with other results of our analyses, the self-energy effects obtained in this study are also given in Table 1.

Regarding the upper panel of Fig. 13 we find hardening or sharpening in samples in which the $2\Delta$ peaks are below or above $\sim 500$ cm$^{-1}$. This indicates that the electronic response, or the coupling to it, or both, weaken in the superconducting state when the gap is above that value. The broadening appears to be at maximum when phonon frequency and $2\Delta$ peak match each other. This is expected, as the phonon will decay most effectively via breaking of a Cooper pair under this condition. That the broadening does not vanish at higher dopings, i.e. at lower peak energies, is a consequence of the $d$-wave shape of the gap function. The disordered film #Ca1, whose self-energy effects are shown in brackets, exhibits a smaller broadening than the two adjacent ordered films. This is directly related to the weaker $B_{1g} 2\Delta$ peak observed in the film #Ca1. Another sample that seems to deviate from the general trend is the fully oxygenated single crystal investigated by Altdorf and Chen. It exhibits a strong broadening of 5.9 cm$^{-1}$ and a high peak energy of 460 cm$^{-1}$. As the renormalized phonon parameters do not depend strongly on the applied description one may speculate that the energy of the $2\Delta$ peak is overestimated in the description employed by Chen et al. in Ref. 26. This could be a consequence of the approximation made in their work in which the frequency dependence of the real part of the electronic response function $R_\epsilon(\omega)$ has been neglected. In fact, if we compare the phonon parameters of the fully oxygenated single crystal of their study with those of the one we studied we find at least two indications that their crystal might have a higher oxygen content. Knowing that the c axis shrinks with increasing oxygen content and that the intermediate broadening, or equivalently, the maximum asymmetry of the $B_{1g}$ phonon shifts to lower temperatures with increasing oxygen content these indications are:

(i) That the renormalized $B_{1g}$ phonon frequency at $\sim 100$ K is 1 cm$^{-1}$ higher in their crystal indicating a slightly smaller c axis. (ii) That the temperature at which they observe the maximum intermediate broadening and the maximum asymmetry is $\sim 70$ K and therefore 10 K lower as in our crystal. As a result of the higher oxygen content we would expect an increased doping and therefore a $B_{1g}$ $2\Delta$ peak below 435 cm$^{-1}$ in their fully oxygenated single crystal compared to the one we studied.

Turning now to the lower panel of Fig. 13 we find hardening or softening for all samples whose $2\Delta$ peaks are below or above the phonon frequency. This corresponds well to the result of a simple picture when the interaction is treated in second order perturbation theory. When the center frequency of the background peak is above the phonon it is shifted downwards and vice versa. A symmetric background peak right on the phonon will yield a vanishing frequency shift. In Fig. 13 the ordered as well as the disordered sample follow the same trend. In the present work only the ordered film #Ca2 shows hardening. However, we have recently revealed the same behavior in disordered Ca-doped samples with higher Ca contents. In 10 % and 15 % doped films we observed $B_{1g} 2\Delta$ peaks of 315 cm$^{-1}$ and 220 cm$^{-1}$ and accompanying hardenings of $\sim 0.2$ cm$^{-1}$ and $\sim 2$ cm$^{-1}$, respectively.

Whereas phonon self-energy effects are often given for a fixed electronic response and varying phonon frequencies, the representation chosen in Fig. 13 is of more practical relevance for at least two reasons. First, because it is easier to vary the doping and therefore the $B_{1g} 2\Delta$ peak by changing the oxygen content than to vary the phonon frequency, and second because the $2\Delta$ peak shifts over a wider energy range than the phonon does. The observed self-energy effects of the $B_{1g}$ phonon principally resemble those seen in theoretical studies. For example we find a maximum in the imaginary part of the self-energy in that energy range where the real part has its maximal slope. However, a more specific comparison with theoretical works is not possible at the moment, as the self-energy effects are a consequence of a coupling to the electronic response function for which a microscopic description is not available at present. Moreover, we have observed that the self-energy-effects are not solely bound to the superconductivity-induced changes of the electronic excitation spectrum. Rather, they appear also in samples which do not exhibit $2\Delta$ peaks in the su-
perconducting state and at temperatures above $T_c$ which will be discussed in the following section. For example, we find a sharpening of 2.5 cm$^{-1}$ and a softening of 1.5 cm$^{-1}$ in the film #Pr2 with an onset around 120 K, where $T_c$ is only 72 K.

C. Electronic Background

The high quality of our fit procedure shows up when $A_{1g}$ and $B_{1g}$ responses are plotted in the same graph as done in Figs. 3 and 7. Evidently, both responses are well-comparable above the $B_{1g}$ 2$\Delta$ peak in the single crystal and the Ca-doped films, even though the strongest phonons appear at substantially different energies in both symmetries. This unpredictable behavior is seen in all films whose dopings are above the optimal value. It gives us additional confidence in the obtained fit parameters.

The doping dependence of the 2$\Delta$ peaks in $A_{1g}$ and $B_{1g}$ symmetry measured at 18 K is depicted in Fig. 4. Beside our data we have again included those obtained by Chen et al. in the graph. In order to determine the doping of their crystals the oxygen contents as well as the $T_c$'s given in the their work have been used in a similar way as described in Sec. 1A. Given as solid lines the gap energies that would correspond to a mean field approach with $2\Delta(p) = 4.28 \, k_B T_c(p)$ where $T_c(p)$ has the parabolic shape given in Eq. (8). Note the reduced energy scale in $A_{1g}$ symmetry.

In agreement with a previous doping-dependent study of Bi-2212 single crystals by Kendziora and Rosenberg we find that the $A_{1g}$ 2$\Delta$ peaks follow - more or less - a parabolic dependence being slightly above that particular curve. However, with the aid of the Pr-doped films our study extends their results towards lower dopings. Note-worthy, the energies of the $A_{1g}$ 2$\Delta$ peaks are almost 100 cm$^{-1}$ lower in the RE-123 samples compared to those of the Bi-2212 single crystals. For example, Kendziora and Rosenberg observe 2$\Delta$ peaks of $\sim$ 400 cm$^{-1}$ near optimal doping. The origin of this behavior is unknown at present. The energies of the $A_{1g}$ 2$\Delta$ peaks of the single crystals shown in Fig. 14 appear to be higher than those of the thin films. However, both groups of samples exhibit a significant scatter of the data. Please note also that the $A_{1g}$ 2$\Delta$ peaks of the single crystals given in Fig. 14 are in fact $A_{1g} + B_{2g}$ 2$\Delta$ peaks as the $B_{2g}$ responses have not been subtracted.

Regarding the doping dependence of the $B_{1g}$ 2$\Delta$ peaks, we find again that the peak energies in the films are smaller than those of the crystals at comparable dopings. The slope of the doping dependence of the film data, however, is well-comparable to the one observed in Bi-2212 single crystals using SIS tunneling and ARPES which is given as a dashed line. This demonstrates a close relationship of the gap values in the Bi-2212 and the RE-123 system that has not been seen so far as high-quality tunneling or ARPES data cannot be obtained in the RE-123 system due to surface problems. Note that in this geometry data at low dopings are not available as the redistributions become unresolvable slightly below the optimal value.

So far, we have not discussed the $B_{2g}$ responses of the films. This is related to our observation that they are not altered with temperature (see, e.g. Fig. 3). In addition, the $B_{2g}$ responses are almost doping independent as shown in Fig. 14(a). In the determination of the $A_{1g}$ efficiencies in those two films #Pr1 and #Pr3 in which we did not measure the $B_{2g}$ spectra we benefitted from this property. Only in the Ca-doped film with the highest doping #Ca2 we observe the evolution of a $B_{2g}$ 2$\Delta$ peak as shown in Fig. 14(b). The energy of $\sim$ 265 cm$^{-1}$ is between those of the $B_{1g}$ and $A_{1g}$ 2$\Delta$ peaks (see Table 1) in agreement with results obtained on similarly doped Bi-2212 single crystals. The intensities of the $B_{2g}$ responses are distinctly smaller than those of the $B_{1g}$ responses with ratios of 0.5 and 0.3 at $\sim$ 700 cm$^{-1}$ in the oxygen- or Pr-doped films and in the film #Ca2, respectively. Near optimal doping the observed ratios of 0.5 are in agreement with those measured on Y-123 single crystals.

We now turn to the doping dependence of the low-temperature electronic responses in $A_{1g}$ and $B_{1g}$ symmetry. Depicted in Fig. 13 are the responses of two under-doped films #Ox1 and #Pr2, the almost optimally doped film #Ox3, and the overdoped film #Ca2 measured at 18 K. The $A_{1g}$ response of the film #Ox1 is not given as it contained significant substrate signal as noted above. In order to improve the signal/noise ratio we have sub-sumed 10 neighboring data points of the original curves yielding, however, a poorer spectral resolution. Three main features can be read from Fig. 13 (1) In contrast to oxygen reduction or Ca doping, Pr doping leads to an increased intensity in the entire energy range. (2) The intensity of the $A_{1g}$ 2$\Delta$ peak is almost independent of the doping provided that filled chains are present. (3) With decreasing doping the $B_{1g}$ 2$\Delta$ peak rapidly loses its strength while shifting to higher energies.

(1) The incoherent background observed in Raman but also in other measurements, like e.g. optical conductivity or resistivity, can be assigned to inelastic scattering of quasi-particles in the CuO$_2$ plane. In this sense the enhanced intensities observed in Pr-substituted samples indicate an enhanced scattering rate. In view of the specific electronic configuration of the Pr$^{3+}$ ion, which can localize holes in the Fehrenbacher-Rice state and in view of its position right in the middle of the copper-oxygen bilayer, an enhanced scattering probability may not be surprising. Interestingly, this enhancement is only observed in $A_{1g}$ and $B_{1g}$ symmetry and not in the $B_{2g}$ symmetry the FS is predominantly sampled close to the diagonals $\pm k_x = \pm k_y$, the former two have significant contributions from the region close to $(\frac{\pi}{a}, 0)$. In view of this behavior our observation suggests that Pr doping may rather amplify already present inelastic scattering near the hot
spots of the FS near \((\pi, 0)\) than add a new scattering channel.

(2) The observation of a rather strong A\(_{1g}\) \(2\Delta\) peak in the underdoped film #Pr2 is in contrast to the behavior seen in Bi\(_{123}\) symmetry. More importantly, it is in contrast to the behavior of the A\(_{1g}\) responses of oxygen-reduced Y-123 single crystals or under- up to almost optimally doped Bi-2212 single crystals, where A\(_{1g}\) \(2\Delta\) peaks have not been observed.

There is a long ongoing debate on the understanding of the gap features in A\(_{1g}\) symmetry observed in cuprate superconductors. Whereas Devereaux et al. initially claimed to obtain a simultaneous description of the electronic responses in A\(_{1g}\), B\(_{1g}\), and B\(_{2g}\) symmetry in a one-band model using Fermi surface harmonics to expand the mass part of the interaction of light with matter for calculations along the Fermi line, they had to admit later that their results depend strongly on the expansion coefficients of the electron-photon vertex which cannot be obtained unambiguously. The same observation was made in a recent theoretical approach in which an integration over the entire Brillouin zone was carried out.

Early on Cardona and co-workers pointed out that the remarkable high intensity of the A\(_{1g}\) response indicates that multiple sheets of the FS are involved in the scattering process. With multiple bands unscreened mass fluctuations can be expected in A\(_{1g}\) symmetry whereas strong screening is expected in a one-band model. In this picture it is difficult to understand why the gap features have similar shapes in different compounds even though the band structures vary significantly. Another argument against the multiple-band picture was the observation of rather strong A\(_{1g}\) \(2\Delta\) peaks in the single layer Tl-2201 close to optimal doping. However, at higher dopings almost vanishing intensities of the A\(_{1g}\) feature and a persisting strong B\(_{1g}\) \(2\Delta\) peak have been observed in Tl-2201. This is in agreement with calculations in which the electronic properties are dominated by a single band.

In our study we still have filled chains in the Pr-substituted underdoped films. Hence, we keep the chain bands which can still provide additional sheets of the FS. This could explain the unaltered intensities of the A\(_{1g}\) \(2\Delta\) peaks seen in the spectra of the Pr-doped samples. That high quality single crystals of optimally doped Bi-2212 \((T_c \approx 95\, \text{K})\) do not show an A\(_{1g}\) \(2\Delta\) peak in contrast to high quality single crystals of optimally doped Y-123 \((T_c \approx 93\, \text{K})\) is another support for our finding that chain-related bands may play a significant role for the Raman response in A\(_{1g}\) symmetry. If we consider the A\(_{1g}\) response to be influenced by the presence of chains, it is likely to assume that the type of oxygen-ordering present in the chain layer will be of some relevance for the shape of the response. The scatter in the energies of the \(2\Delta\) peak close to optimal doping seen in Fig. 14 could be related to this particular order. Moreover, one might interpret the significantly higher intensities of the \(2\Delta\) peaks seen in the study of the single crystal (see Fig. 8) as evidence for an increased oxygen-order in the chain layer in view of the disorder-related reduction of \(2\Delta\) peak intensities shown in Fig. 11.

(3) When the intensities of the \(2\Delta\) peaks decrease with decreasing doping, a structureless background remains in B\(_{1g}\) symmetry. In contrast to the film #Pr2, where additional background intensity is observed as already discussed, the oxygen-reduced film #Ox1 exhibits comparable intensities at low \((\sim 100\, \text{cm}^{-1})\) and high \((\sim 800\, \text{cm}^{-1})\) Raman shifts, showing a slightly rising background.

The nature of the low-energy Raman response has been the subject of various experimental and theoretical investigations. Concerning B\(_{1g}\) symmetry the following observations have been made: (i) Whereas the low-energy B\(_{1g}\) response in the antiferromagnetic precursors can be attributed to two-magnon excitations in a good approximation, the two-magnon excitations lose and incoherent excitations gain strength with increasing doping. (ii) In optimally or slightly underdoped Bi-2212 single crystals the slope for \(\omega \rightarrow 0\) cannot be described in a Drude-like picture in contrast to the response in B\(_{2g}\) symmetry. (iii) In slightly overdoped Y-123-O\(_{6+y}\) single crystals with \(y \approx 1\) the temperature dependence of the B\(_{1g}\) response at small Raman shifts is not simply following the behavior expected in the frameworks of the marginal or the nested Fermi liquids. (iv) The response, which does not depend on the excitation energy in moderately doped superconductors, becomes resonantly enhanced at very high doping levels exhibiting a resonance position similar to that observed for two-magnon excitations at lower doping levels.

In view of the above results it has been suggested that the B\(_{1g}\) response consists at least of three different contributions in the investigated doping range. A magnetic contribution due to overdamped two-magnon excitations, which persist in the superconducting state, an electronic contribution resulting from incoherent quasiparticle scattering, and a mixed spin-charge response which appears below the pseudogap temperature. Recently, we have observed that magnetic scattering vanishes at high dopings \(p \geq 0.21\) in Bi-2212 single crystals. Here, we didn’t investigate samples with such high dopings, therefore we can assume that two-magnon excitations are always present in the B\(_{1g}\) efficiencies at low temperatures, having increasing weight at lower dopings. Apparently, when the magnetic contributions strengthen below optimal doping the B\(_{1g}\) \(2\Delta\) peaks vanish concomitantly in RE-123 compounds. In Bi-2212 compounds weak pair-breaking-like excitations have been observed even at low dopings. They appear around 600 cm\(^{-1}\) and it was reported that they are also present above \(T_c\). A detailed investigation of that frequency region is hindered in this study by the presence of a disorder-induced infrared-active phonon at 590 cm\(^{-1}\) (see Fig. ). In contrast to a previous study of a Y-123-O\(_{6.5}\) single crystal the B\(_{1g}\) responses at large Raman shifts above 700 cm\(^{-1}\) remain almost dopings independent in the oxygen-doped films down to \(y=0.52\) in
the film #Ox1 in our study. This may be related to the fact that we had to subtract substrate signal in this film, as we cannot exclude residual substrate intensity. In fact, two strong substrate modes are still observed in the 18 K efficiency (see Fig. [7]).

D. Peculiarities of the Electronic Response

In this section we will consider two peculiarities of the electronic response unveiled in this study. One of these is the doping dependence of the exponent of the low-frequency power laws in $A_{1g}$ and $B_{1g}$ symmetry and another the influence of disorder on the strength and energy of the $2\Delta$ peaks.

(i) As shown in Table I the $A_{1g}$ responses fall off as $\omega^{1.0 \pm 0.15}$ and no systematic dependence on the doping is observed. In contrast, the exponents observed in $B_{1g}$ symmetry increase systematically with doping. In detail, we observed a slope $\sim \omega^{1.2}$ in the underdoped film #Ox1, $\sim \omega^{0.5}$ in the almost optimally doped film #Ox3, and $\sim \omega^{1.7}$ in the overdoped film #Ca2. In slightly overdoped films even a change of slope was observed appearing around $270 \text{ cm}^{-1}$ (see Secs. III B and IV B). Above that frequency higher exponents of $\omega^{3.0}$ and $\omega^{2.9}$ are observed in the film #Ox4 and the single crystal #sc, respectively. A similar crossover has been observed in a previous investigation of the electronic responses in differently doped Y-123 single crystals.

The relevant power laws in Raman spectra of cuprate superconductors are those at small Raman shifts. They may be compared with theoretical estimates obtained in $\omega/(2\Delta)$ expansions of the calculated electronic responses. Assuming $d$-wave symmetry of the order parameter Devereaux et al. obtained power laws $\sim \omega$ and $\sim \omega^3$ in $A_{1g}$ and $B_{1g}$ symmetry, respectively. Those have in fact been observed in case of optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ and identified as support for the $d$-wave scenario.

The power laws of the $B_{1g}$ responses in our study clearly deviate from the value expected for a $d$-wave superconductor. The deviation and its doping dependence cannot be accounted for with present theories and pose some constraints on any models of the Raman response.

(ii) The influence of disorder on the strength and energy of the $2\Delta$ peaks has not been established before. The reduced intensities observed in this study are in agreement with theoretical expectations. However, a quantitative analysis of the strength of the scattering rates lies beyond the scope of this work. Beside diminished intensities we also observed shifts of the energies of the $2\Delta$ peaks when comparing the disordered with ordered films (see Table I). Whereas the peaks shifts towards higher energies in the slightly overdoped film #Ca1, a down shift of the $A_{1g}$ $2\Delta$ peak is observed in the underdoped film #Pr1 in which a $B_{1g}$ $2\Delta$ peak could not be identified. Based on the doping dependence of the $2\Delta$ peaks shown in Fig. [4] one can assign decreased doping levels to the disordered films compared to the ordered ones. This assignment agrees with their respective critical temperatures which have already been interpreted as indications for reduced doping levels in Sec. VI A.

E. Electron-Phonon Coupling and Intensity Anomalies

Our description of phonon and interacting background according to Eqs. (3) and (6) allows us to obtain the mass-enhancement factor $\lambda$ as well as a measure of the effective electron-phonon coupling constant $g$. They are determined from the fit parameters via the relations

$$\lambda = 2R_s(\omega_p)/C \cdot \omega_p \quad \text{and} \quad g^2 \sim I_{\infty}/C.$$ 

In contrast to $I_{\infty}/C$, the quantity $\lambda$ is not useful in the superconducting state as additional self-energy contributions due to the pair-breaking excitations appear. However, in the normal state both quantities are clearly correlated as seen in Figs. [6] and [14] where instead of $\lambda$ the ratio $R_s(\omega_p)/C = 2.5 \text{ cm}^{-1}$ yielding $\lambda = 0.015$ when a typical bare phonon frequency $\omega_p = 344 \text{ cm}^{-1}$ is taken. This value is slightly below $\lambda = 0.021$ calculated by Rodriguez et al. using a linear muffin-tin-orbital frozen-phonon calculation. Somewhat higher values of the coupling with $\lambda = 0.056$ are used in the work of Devereaux et al. in order to explain the line shape of the $B_{1g}$ phonon in slightly overdoped Y-123. In contrast to our approach, they use a microscopic description of the imaginary part of the electronic response, taking impurity and electron-electron scattering into account as proposed in the theory of the nested Fermi liquid. For their description of the background three fit parameters are required instead of the two, $I_{\infty}$ and $\omega_T$, we use. Moreover, they describe the phonon using five fit parameters while we only have four: $\omega_p$, $\Gamma$, $C$, and $R_0$. Their fit formula is identical to our Eq. (6) in the limit of a strongly interacting phonon but differs in the case of an only weakly interacting, symmetric one. An additional difference between both descriptions is that Devereaux et al. do not consider the frequency dependent real part of the electronic response in their description but use $\lambda$ as an independent fitting parameter in order to describe the asymmetry of the phonon. As their spectra are well-comparable to our thin film and single crystal data, the origin of the deviating coupling strengths is not obvious. It will most likely be related to the different degrees of freedom allowed in both approaches.

In our study a decreasing coupling is observed in the oxygen-doped films with decreasing doping. In detail, we find $R_s(\omega_p)/C = 2.54 \text{ cm}^{-1}$ and $R_s(\omega_p)/C = 0.09 \text{ cm}^{-1}$ in the films #Ox4 and #Ox1 at 100 K, corresponding to $\lambda = 0.015$ and $\lambda = 0.0005$, respectively. The same trend has recently been observed in a single crystal study by Opel et al., in which the microscopic approach of Devereaux et al. was employed. However, they need
again significantly higher values of the coupling to describe their spectra, even though these spectra are well-comparable to our thin film data. To give an example, they use $\lambda = 0.026$ to describe the $B_{1g}$ spectrum of an underdoped Y-123-O$_{6.5}$ single crystal which exceeds our estimate by a factor of 50. In addition to the higher degree of freedom allowed in the approach of Devereaux et al.\cite{118}, this difference may also be related to the somewhat different descriptions used in the limit of weakly interacting, symmetric phonons. Clearly, this large discrepancy demands to be resolved.

In contrast to oxygen reduction, Pr substitution yields only weakly decreasing coupling constants as seen in Fig. 10. However, at high Pr concentrations, which are not shown here, the $B_{1g}$ phonon becomes symmetric, and $\lambda$ approaches zero in Pr-123 films.\cite{118}

To illustrate the doping dependence of the electron-phonon coupling in oxygen- and Ca-doped films in the the superconducting state we show in Fig. 17 the Raman efficiencies in $B_{1g}$ symmetry measured at 18 K. The doping increases from top to bottom and the determined couplings $I_{\infty}/C$ are given for each spectrum. Whereas we observe a strong, sharp, and symmetric $B_{1g}$ phonon in the film #Ox1, the mode is weak, broad, and asymmetric in the film #Ca2. Apparently, the disorder-induced modes at 230 cm$^{-1}$ and 590 cm$^{-1}$ appear and grow with decreasing oxygen content. This has been used in Sec. VI A to determine the oxygen contents of the films #Ox2 and #Ox3, where, however, room-temperature data have been considered as these modes exhibit reduced intensities (bleaching) at lower temperatures.\cite{21, 106}

The decreasing effective couplings at low dopings as observed in Figs. 1, 14, or 17 have to be discussed with respect to the assumptions which have been made in Sec. III A in order to arrive at the description of the Raman efficiency in Eq. (9). There, we have explicitly assumed that the phonon gets renormalized by the electronic response function whose imaginary part is observed in the Raman spectrum. As mentioned in Sec. VI C we can assume that the electronic response in $B_{1g}$ symmetry consists of incoherent electronic and two-magnon excitations as well as a spin-charge response. Especially, the two-magnon contribution will grow with decreasing doping. The symmetric appearance of the $B_{1g}$ phonon in the antiferromagnetic precursors Y-123-O$_6$ (Ref. 118) or Pr-123 (Ref. 76) indicates that this mode is not interacting with two-magnon excitations, at least not with those at low energies which originate from the vicinity of the Brillouin zone. The reduced effective coupling at low dopings therefore expresses at least partly the overestimation of the background contribution responsible for the observed self-energy effects. Support for this picture is our observation that we find mass-enhancement factors which correspond fairly well to the results of the LDA-type calculation of Rodriguez et al.\cite{111} at higher dopings, where the two-magnon excitations diminish. However, in addition to the above considerations it is likely to assume that the density of states at the hot spots, which are sampled in $B_{1g}$ symmetry, will affect the electron-phonon coupling as well. The density will increase strongly at high dopings as the van Hove singularity moves closer to the Fermi level. Another origin for reduced effective coupling strength

The fact, that the effective coupling of Pr-doped films is stronger at comparable dopings than the one in oxygen-reduced films may indicate that the low-energy magnetic contributions are growing weaker with Pr-substitution. It may also be related to an enhancement of the coupling strength induced by the Fehrenbacher-Rice state of the Pr atom.

During the presentation of the self-energy effects we have stressed the finding that the effective coupling $I_{\infty}/C$ appears to be related to the bare phonon intensity $I_{phon}$ in the sense that both show anomalies at similar temperatures. In detail, we find that $I_{\infty}/C$ is maximal near the temperature at which $I_{phon}$ is minimal at higher dopings or changes slope at lower dopings. As stated earlier $I_{phon} = \frac{\pi}{C} R_0^2$ is proportional to $g_{pp}^2$, where $g_{pp}$ describes the coupling of the phonon to interband electronic excitations. $I_{\infty}/C$, on the other hand, is proportional to $g^2$, i.e. to the coupling of the phonon to intraband electronic excitations. Our observations therefore indicate an intimate relation between both excitation channels. To demonstrate this relation we display the ratio $(I_{\infty}/C)/I_{phon} = \frac{\pi}{C} (\frac{1}{R_0^2} \propto (g/g_{pp})^2$ versus temperature in Fig. 18. This ratio reflects the asymmetry of the phonon line shape: The higher the ratio, the higher the asymmetry. For each sample the obtained ratios are normalized to their maximal values. The flat vertical bar represent the temperatures at which the ratio is at maximum and to which we will refer as $T_{anomaly}$ in the following. Neither in the highest doped film #Ca2 nor in the one with the lowest doping #Ox1 a clear maximum is observed. In the former (latter) we find that the ratio grows (decreases) continuously with decreasing temperature. In the other films $T_{anomaly}$ increases in a monotonic fashion with decreasing doping. In the films #Ox2 and #Ox3 $T_{anomaly}$ represents rather a change of slope than a clear maximum. Importantly, we find that $T_{anomaly} > T_c$ below optimal doping. This is indicated in the inset, where in addition to $T_{anomaly}$ the parabolic dependence of the critical temperature according to Eq. (6) with $T_{c,max} = 90$ K is given. Apparently, the origin of the varying coupling ratios is not a superconductivity-induced effect. However, in the film #Ox4 we find $T_{anomaly} = 62 \pm 6$ K which corresponds well to the temperature interval at which the $B_{1g}$ $2\Delta$ peak passes the phonon as shown in Fig. 2. This, in turn, suggests a connection with the superconducting gap as proposed earlier.\cite{113}

In the simple Fano fit according to Eq. (3) the asymmetry of the phonon is proportional to the inverse of the Fano parameter $q$. Hence, a maximum value of the ratio depicted in Fig. 18 would correspond to a minimal value of the Fano parameter. Using the simple Fano formula Altendorf et al.\cite{84} studied the $B_{1g}$ phonon in dif-
ferrily doped Y-123-\textsubscript{O\textsubscript{6+y}} single crystals. In agreement with our results they observe that the asymmetry (1/q) exhibits a maximum as a function of temperature but could only resolve it in samples with oxygen contents y \geq 0.85. They find, that the temperature at which the maximum appears shifts to higher values with decreasing doping. These temperatures correspond to the anomaly temperatures T\textsubscript{anomaly} defined in this study. At a particular doping, the anomaly temperatures are higher in the crystals than in the films which might be correlated to the observation that the B\textsubscript{1g} 2\Delta peaks of the crystals exceed those of the films at a particular doping level (see Fig. 14).

In addition to the anomalies with respect to intensity and coupling, we noted in Sec. VII B that self-energy effects already started to appear above T\textsubscript{c} in all films whose doping levels are below the optimal value. These self-energy effects cannot be related to background redistributions, especially, not in the underdoped films #Ox1, #Pr1, and #Pr2 in which B\textsubscript{1g} 2\Delta peaks have not been observed. The question arises whether the self-energy effects observed above T\textsubscript{c}, i.e. softening and sharpening, can be an indication of a lattice distortion occurring at T\textsubscript{anomaly}. In this case we would expect to observe indications of the distortion in all other modes as well. As this is not the case in the films #Ox1, #Ox2, #Pr2, and #Pr3 we conclude that the self-energy effects as well as the anomalies with respect to coupling and intensity in the underdoped films originate from the interaction with electronic excitations which are not directly observed in the Raman spectra. Possible candidates for these excitations are those which are known to become strongly suppressed below the pseudogap temperature T\textsuperscript{*} in underdoped cuprates.

Suppressions of gap-like structures have been observed with NMR, specific heat, resistivity, optical conductivity, ARPES, SIS tunneling, or scanning tunneling microscopy. They have also been reported in previous Raman studies in which the B\textsubscript{1g} 2\Delta peaks were not observed. The appearance of these electronic excitations is not or only weakly Raman-active in the RE-123 system.

Recent ARPES experiments helped to clarify the k and T dependence of the pseudogap. The following picture emerges from these studies: At T = T\textsuperscript{*} a gap opens up at the FS crossings along the (\frac{\pi}{a}, 0) to (\frac{\pi}{a}, \frac{\pi}{a}) direction. With decreasing temperature the gap value increases and spreads out over the FS. Simultaneously, the non-gapped regions of the FS, so-called “Fermi arcs”, shrink and collapse into the point node of the d\textsubscript{x\textsuperscript{2}−y\textsuperscript{2}}-wave gap at T = T\textsubscript{c}. The energy of the superconducting gap observed at the FS crossings below T\textsubscript{c} evolves smoothly from the values of the pseudogap observed above T\textsubscript{c} (see lowest panel in Fig. 19). No pseudogap features are observed in the normal state in overdoped samples.

Coming back to our observations one may assume that T\textsubscript{anomaly} is that temperature at which the gap or the pseudogap is passing the phonon. The doping dependence of T\textsubscript{anomaly} as seen in Fig. 18 yields strong support for this assumption, which we have already presented in a previous work. In order to clarify this point let us consider the temperature dependence of the gap that we can read out of our data. We will restrict ourselves to the energy of the maximum gap which appears near (\frac{\pi}{a}, 0) as these regions are probed with preference in Raman experiments carried out in B\textsubscript{1g} symmetry. In fact, the B\textsubscript{1g} 2\Delta peak has been identified with the maximum value of a d\textsubscript{x\textsuperscript{2}−y\textsuperscript{2}} gap in various theoretical treatments of the Raman response. As a measure of the temperature at which the gap closes around (\frac{\pi}{a}, 0) we can use T\textsuperscript{*} in conformity with the ARPES results. In order to connect the B\textsubscript{1g} 2\Delta peaks with the pseudogap temperature we will use a simple straight line which reflects the ARPES results to a good approximation. The obtained graphs for the ordered films are depicted in Fig. 19. In the upper panel we show the results of the oxygen doped films which exhibited 2\Delta peaks. The grey horizontal bar represents the energy of a typical renormalized B\textsubscript{1g} phonon frequency of 342 cm\textsuperscript{-1}. The open symbols on this bar represent the anomaly temperatures of the respective films. In accordance with our assumption, they are located close to the intercepts of the linear extrapolations that connect the 2\Delta peaks observed near T\textsubscript{c} with the respective pseudogap temperatures in the films #Ox2 and #Ox3. Interestingly, we observe 2\Delta peaks with energies below the phonon frequency in the film #Ox4. Here, we find that T\textsubscript{anomaly} lies right in that temperature range in which the 2\Delta peaks pass the phonon frequency. In the middle panel the data of the ordered Pr- or Ca-doped films are depicted. As mentioned earlier, the 2\Delta peaks in the film #Ca2 are below the phonon frequency for all temperatures. This is in agreement with our inability to identify T\textsubscript{anomaly} in this film. The data for the film #Pr3 correspond well to the observations in the oxygen-doped samples. As we did not observe any 2\Delta peaks in the film #Pr2 only T\textsubscript{anomaly} and T\textsuperscript{*} are given for this sample.

In the lowest panel of Fig. 19 leading edge shifts determined by Harris et al. from an analysis of ARPES data are reproduced. The ARPES spectra have been taken on an underdoped T\textsubscript{c} = 85 K Bi-2212 single crystal at the FS crossings along the (\frac{\pi}{a}, 0) to (\frac{\pi}{a}, \frac{\pi}{a}) direction. They represent a measure of the gap value. Apparently, these data closely resemble those of the underdoped T\textsubscript{c} = 87 K film #Ox1 in the upper panel. Regarding the different energy scales one has to take into account that ARPES measures \Delta instead of 2\Delta and that the leading edge shift is given instead of the gap value.

The data depicted in Fig. 19 suggest strongly that the enhanced ratios (g/\textsubscript{pp})\textsuperscript{2} observed at T\textsubscript{anomaly} have a quasi-resonant origin. The appearance of a resonance in the bare phonon contribution I\textsubscript{phon} = \pi A\textsubscript{pp}\textsuperscript{2} is in agree-
ment with the assignment of $g_{pp}$ to the vertex which couples the phonon to intraband electronic excitations given in Sec. IIIA. This abbreviated “photon-phonon” vertex explicitly allows resonances to occur as it involves $A \cdot p$ transitions. A superconductivity-induced increase of the interband contribution to the Raman intensity of the $B_{1g}$ phonon has been obtained in a theoretical treatment of the scattering process by Sherman et al.\cite{Sherman2002} The latter authors showed that the increase will depend on the doping level, becoming stronger in underdoped samples. This appears to be in agreement with our data. Our results, however, also indicate that there is an intimate relation between the intensity anomaly due to the interband contribution and the relative energies of phonon and $B_{1g}$ $2\Delta$ peak which has not been observed before. We find that the resonance in $I_{phon}$ vanishes as soon as the phonon energy is above $2\Delta(T=0)$.

In IR Raman measurements of underdoped Y-123 with $T_c \leq 84$ K, an anomalously increasing intensity of a broad low-energy electronic feature has been observed below $T^*$\cite{Kivelson1993} The feature is assigned to an interband excitation which involves $A \cdot p$ transitions. On the basis of our results we predict that the anomaly will vanish at higher dopings when $2\Delta < 500$ cm$^{-1}$.

The resonance with respect to the effective coupling could have two different origins. First, it can simply occur because the background contribution at the phonon frequency becomes maximal when the gap value equals the phonon energy, or second, it may indicate that the electron-phonon coupling itself becomes resonantly enhanced. The first can only be expected as long as $2\Delta$ peaks are observed. In the underdoped films, however, we observe a structureless response which is not altered within the noise level for all temperatures. The second argument would indicate a breakdown of Migdal’s theorem which allows one to neglect vertex corrections to the electron-phonon coupling in a metal.\cite{Migdal1958} Whether cuprate HTS are a class of materials where such a breakdown could occur is currently under debate in view of recent experiments which indicate that polaronic charge carriers are present in superconducting La$_{2-x}$Sr$_x$CuO$_4$\cite{Kivelson1993} That the $B_{1g}$ phonon interacts with the pseudogap in the observed way is most likely related to the fact that the electron-phonon vertex, which has been obtained in a first approximation by Devereaux et al.\cite{Devereaux1995} samples the FS with preference along the $k_x$ and $k_y$ directions. Hence, it will be most sensitive to the maximum value of the gap which appears in these regions.

As a $B_{1g}$ plane oxygen phonon is present in all cuprates with more than one CuO$_2$ plane in the unit cell, we predict that phonon anomalies will also be observed in these compounds when the $2\Delta$ peak merges the phonon frequency. The effect will be smaller in those compounds in which the planes are not buckled.

VII. CONCLUSION

We have investigated laser-deposited c-axis oriented Y$_{1-x}$(Pr,Ca)$_x$Ba$_2$Cu$_3$O$_{6+y}$ thin films using Raman and transport measurements, and the Raman spectra of an YBa$_2$Cu$_3$O$_7$ single crystal. Variations of the Pr, the Ca, or the chain-oxygen content allow us to achieve different doping levels ranging from under- to overdoped. Using a previously presented description of the Raman response we are able to deconvolute electronic and phononic excitations. This allows us to identify the $2\Delta$ peaks appearing below $T_c$ even in the presence of strongly interacting phonons. Whereas we observe that the energy of the $A_{1g}$ $2\Delta$ peak follows $T_c$, the peak energies in $B_{1g}$ symmetry increase monotonically with decreasing doping. As the $B_{1g}$ $2\Delta$ peaks are measures of the maximum value of a $d_{x^2-y^2}$-wave gap, the latter result is in qualitative agreement with the trends obtained in SIS-tunneling or ARPES studies of Bi-2212 single crystals where this non-mean field behavior has already been established. At low dopings the $B_{1g}$ $2\Delta$ peaks become un-resolvable. The $A_{1g}$ $2\Delta$ peaks, however, are still observed at low dopings in Pr-doped films in contrast to previous results obtained in oxygen-reduced samples. We relate this finding to persisting chain-related bands which inhibit a screening of the $A_{1g}$ response expected in one-band models of the Raman response. In Pr-doped films we find enhanced scattering intensities for all frequencies in $A_{1g}$ as well as in $B_{1g}$ symmetry compared to the oxygen- or Ca-doped films. We attribute this observation to quasi-particles scattering at the Pr atoms where Pr $4f$ orbitals have hybridized with adjacent oxygen 2$p$ orbitals into the Fehrenbacher-Rice state. In disordered Pr- and Ca-doped films we observe weakenings of the superconductivity-induced features accompanied by decreased dopings.

Regarding phononic excitations we focus in this work on the $B_{1g}$ phonon at 340 cm$^{-1}$, a mode which involves out-of-phase vibrations of the plane-oxygen atoms. This mode interacts strongly with low-lying electronic excitations and hence, exhibits an asymmetric Fano-type line shape. Our description of the $B_{1g}$ phonon enables us to identify the self-energy contributions due to the electronic response and, especially, yields measures of the effective electron-phonon coupling. One of these measures is the mass-enhancement factor $\lambda$ which is found to agree well with LDA expectations for samples near optimal doping. Whereas the observed self-energy effects are in qualitative agreement with the relative positions of $B_{1g}$ $2\Delta$ peak and phonon frequency, they cannot completely be attributed to the redistribution of the electronic response appearing below $T_c$. Moreover, renormalizations above $T_c$, which we have observed below optimal doping, strongly indicate that the phonon also interacts with excitations which become gapped in the pseudogap phase. It turns out that these excitations are not directly observed in the Raman spectra. However, we find that the
temperature at which the pseudogap passes the phonon can be identified as that one at which the phonon is maximal asymmetric. Using our model we find that the ratio of the electron-phonon coupling constants to intra- and interband electronic excitations is at maximum at that temperature. Pseudogap temperatures $T^*$ determined from transport measurements, temperatures of maximum asymmetry, and $B_{1g} 2\Delta$ peaks yield temperature dependent gaps for our films which closely resemble those seen in ARPES measurements at the FS crossings along the $(\pi/a, 0)$ to $(\pi/a, \pi/a)$ direction.

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From an analysis of Figs. 3 – 5 we obtain penetration depths \( l = 73 \text{ nm} \) and \( l = 78 \text{ nm} \) for \( y = 1 \) and \( y = 0.5 \), respectively at \( \lambda_{\text{las er}} = 458 \text{ nm} \).

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The Hilbert transformed incoherent contribution is:

\[ R_{\text{inc}}(\omega) = i \omega \left[ 0.5 + \frac{1}{2} \ln(\omega_{\text{cut}}/\omega_T) + \sqrt{2} \arctan(\eta - 1) \right], \]

where \( \eta = \tanh(\omega/\omega_T) \).

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The probability to have an interrupted chain at a particular oxygen content \( y \) can be described by:

\[ P(y) \approx 0.484y - 5.285y^2 + 79.391y^3 - 177.29y^4 + 138.85y^5 - 36.131y^6 \text{ for } 0 \leq y \leq 1. \]

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FIG. 1. Temperature dependence of the in-plane resistivity of the investigated $Y_{1-x}(\text{Pr, Ca})_x\text{Ba}_2\text{Cu}_3\text{O}_{6+y}$ films.

FIG. 2. Illustration of the fit parameters. In the left panel on the top an artificial efficiency consisting of an interacting phonon as well as of an electronic response is shown. Below, the interacting phonon contribution, proportional to $(1/C)$, with renormalized parameters is displayed. At the bottom, the non-interacting phonon contribution, proportional to $R_0^2/C$, with bare phonon parameters is given. The electronic response used to obtain the interacting phonon contribution is shown in the top row of the right panel. Below, the two Lorentzians describing the redistribution of the background are displayed. The $2\Delta$ peak is described with the frequency $\omega_{2\Delta}$ and the linewidth (HWHM) $\Gamma_{2\Delta}$. The intensities of the peak and the suppression are $I_{2\Delta}$ and $I_{\text{supp}}$, respectively. At the bottom, the hyperbolic tangent with crossover frequency $\omega_T$ and intensity $I_\infty$ is shown. The offsets of the contributions are indicated by horizontal lines.

FIG. 3. Raman efficiencies of the film #Ox4 in $A_{1g}$, $B_{1g}$, and $B_{2g}$ symmetry taken at $T = 152$ K (solid lines) and 18 K (dots). Raman-active phonons are indicated. The efficiencies are offset as given in brackets.

FIG. 4. (a): $A_{1g}$ symmetry. In the uppermost spectrum the Raman efficiency $I_0(\omega)$ of the film #Ox4 taken at $T = 18$ K (dots) and the fit result (solid line) are shown. Below, the fitted phonon profiles (solid line), the electronic response $g_\ast(\omega)$ obtained after subtraction of the phonons (dots), and the numerically determined real part of the electronic response function $R_\ast(\omega)$ (dots) are given. The analytical descriptions of the response used in the fit are included as solid lines. The spectra are offset as given in brackets, all intensities are given in the same units. (b): The corresponding data in $B_{1g}$ symmetry.

FIG. 5. Electronic responses $g_\ast(\omega)$ of the film #Ox4 in $A_{1g}$ and $B_{1g}$ symmetry at various temperatures. The dashed lines indicate the energies of the fit parameter $\omega_{2\Delta}$ at $T = 18$ K. In the right panel the frequency of the $B_{1g}$ phonon is given as a dashed line. The spectra are offset for clarity.

FIG. 6. Electronic responses $g_\ast(\omega)$ of the oxygen-doped films in $A_{1g}$ and $B_{1g}$ symmetry at $T = 18$ K. The dashed lines indicate the energies of the fit parameter $\omega_{2\Delta}$ of the film #Ox4 in the respective symmetries at $T = 18$ K. The spectra are offset as given in brackets.

FIG. 7. Temperature dependence of fit parameters of the $B_{1g}$ phonon for the oxygen-doped films and the single crystal. Doping increases from left to right. Closed circles represent the bare phonon parameters $\omega_p$, $\Gamma$, and $I_{\text{phon}}$, open circles the renormalized values $\omega_p$, $\gamma_p$ and $I_{\text{tot}}$. Diamonds and crosses are the self-energy contributions $R_\ast(\omega_p)/C$ and $g_\ast(\omega_p)/C$, respectively. Dashed lines are fits to an anharmonic decay, solid ones are guides to the eye. Also shown is the ratio $I_\infty/C$ (closed squares). Dash-dotted lines indicate the respective $T_c$’s of the films and the single crystal. Some data are scaled as given in brackets. Marker sizes represent the vertical accuracies.

FIG. 8. (a): Raman efficiencies $I_0(\omega)$ of the single crystal in $A_{1g} + B_{2g}$ $[z(x'x')^z]$ and $B_{1g}$ symmetry taken at $T = 12$ K. (b): Electronic responses $g_\ast(\omega)$ obtained after subtraction of the phonons.

FIG. 9. Electronic responses $g_\ast(\omega)$ of the ordered substituted films in $A_{1g}$ and $B_{1g}$ symmetry at $T = 18$ K. The dashed lines indicate the energies of the fit parameter $\omega_{2\Delta}$ of the film #Ox4 in the respective symmetries at $T = 18$ K. The spectra are offset as given in brackets.

FIG. 10. Temperature dependence of the fit parameters of the $B_{1g}$ phonon for the substituted films. Doping increases from left to right. Columns of the disordered films have a grey background. Closed circles represent the bare phonon parameters $\omega_p$, $\Gamma$, and $I_{\text{phon}}$, open circles the renormalized values $\omega_p$, $\gamma_p$ and $I_{\text{tot}}$. Diamonds and crosses are the self-energy contributions $R_\ast(\omega_p)/C$ and $g_\ast(\omega_p)/C$, respectively. Dashed lines are fits to an anharmonic decay, solid ones are guides to the eye. Also shown is the ratio $I_\infty/C$ (closed squares). Dash-dotted lines indicate the respective $T_c$’s of the films and the single crystal. Some data are scaled as given in brackets. Marker sizes represent the vertical accuracies.

FIG. 11. Electronic responses $g_\ast(\omega)$ of the order-disorder pairs with 20 % Pr and 5 % Ca content in $A_{1g}$ (dotted line) and $B_{1g}$ (solid line) symmetry at $T = 18$ K. All four panels have the same frequency and intensity range.

FIG. 12. Normalized resistivities $[\rho(T) - \rho(O)]/\alpha T$ as a function of temperature, where $\alpha$ is the slope of the $T$-linear region of $\rho(T)$ and $\rho(0)$ is the extrapolated value to $T = 0$ K.
FIG. 13. Self-energy effects of the investigated films (solid circles) as well as of single crystals (open circles) versus energy of the $B_{1g}$ $2\Delta$ peak. In the upper (lower) panel the broadening (frequency shift) relative to the anharmonic decay for the data points at the lowest temperatures are given. Results of studies in which the $2\Delta$ peaks and the self-energy effects of identical single crystals have been obtained separately by Chen et al. and Altendorf et al., respectively, are included. The dotted lines are guides to the eye and the grey vertical bar indicates a typical phonon frequency of $\omega_v = 342$ cm$^{-1}$. The data of the disordered film #Ca1 are given in brackets.

FIG. 14. Doping dependence of the $2\Delta$ peaks of the investigated films (solid circles) as well as of single crystals (open circles) in $A_{1g}$ and $B_{1g}$ symmetry at $T = 18$ K. Single crystal data of Chen et al. are also included. Solid lines represent a standard BCS mean-field $d$-wave prediction with $2\Delta = 4.28\, k_B T_c$, shown to highlight the non-mean-field trend of the $B_{1g}$ data. The dashed line describes the doping dependent gap $2\Delta$ in Bi-2212 obtained from an analysis of ARPES and tunneling in Ref. 12.

FIG. 15. Doping dependence of the electronic responses $\rho_\ast(\omega)$ of the underdoped films #Pr2 and #Ox1, the optimally doped film #Ox3, and the overdoped film #Ca2 in $A_{1g}$ and $B_{1g}$ symmetry at $T = 18$ K. In order to reduce the noise, 10 neighboring data points of the original spectra have been averaged for this graph yielding a spectral resolution of $\approx 20$ cm$^{-1}$.

FIG. 16. (a): Comparison of the $B_{2g}$ Raman efficiencies $I_0(\omega)$ of the films #Pr2 and #Ox3 taken at 18 K. (b) Electronic response $\rho_\ast(\omega)$ in $B_{2g}$ symmetry of the film #Ca2 at 18 K (solid line) and 102 K (dotted line). The dashed line indicates the energy of the fit parameter $\omega_{2\Delta}$ at $T = 18$ K.

FIG. 17. Doping dependence of the Raman efficiencies $I_0(\omega)$ in $B_{1g}$ symmetry taken at $T = 18$ K. Arrows indicate phonons of the substrate which remained after subtraction of the substrate signal. For each sample the respective effective coupling constant $I_\infty/C$ is given. The dashed line indicates a typical phonon frequency of 342 cm$^{-1}$. The spectra are offset as given in brackets.

FIG. 18. Normalized ratio of the square of the coupling constants $g$ and $g_{pp}$ versus temperature. Doping decreases from top to bottom and open circles and crosses are used alternately for clarity. Left panel: oxygen-doped films and single crystal, right panel: substituted films. Fat bars indicate temperatures $T_{anomaly}$ at which the ratio is either at maximum or changes slope. Dotted lines represents the maximum transition temperature of the films $T_{c,max} = 90$ K. Data are offset as given in brackets. In the inset $T_{anomaly}$ is given versus doping. The open square corresponds to the single crystal and closed ones to the films. The data point of the film #Ca2 is given as an extended rectangle. Also shown in the inset is a $T_c(p)$ curve obtained according to Eq. (6) with $T_{c,max} = 90$ K.

FIG. 19. Energy of the gap $2\Delta$ near $(\frac{\pi}{a},0)$ determined by the fit parameters $\omega_{2\Delta}$ in $B_{1g}$ symmetry and $T_\ast$ (closed symbols) versus temperature. A zero gap energy is indicated by a dotted line and a gap energy of 342 cm$^{-1}$ by a grey bar. Open symbols on the grey bar represent $T_{anomaly}$ of the respective films. In the lower panel ARPES results of the shifts of the leading edge midpoints relative to the Fermi energy at the FS crossing near $(\frac{\pi}{a},0.2\frac{\pi}{a})$ taken from Ref. 19 are depicted. These data have been obtained on an underdoped Bi-2212 single crystal and represent a continuously decreasing gap.
TABLE I. Names and properties of the investigated $Y_{1-x}(Pr, Ca)_x Ba_2 Cu_3 O_{6+y}$ films with nominal Ca or Pr contents $x$ and cool down oxygen-partial pressures $p_{ox}$. The film thicknesses are determined from the deposition parameters. All films are deposited on 1 mm thick SrTiO$_3$(100) substrates. $\rho$, $T_c$, and $T^*$ are the resistivity, the critical temperature, and the pseudogap temperature, respectively. $p$ is the doping level and values determined from the Ca, Pr, and oxygen content as well as values determined according to Eq. (8) are given. In this study the mean value $\bar{p}$ is used.

| Film  | Thickness (nm) | $x$ | $p_{ox}$ (mbar) | $y$ | $\rho(100\,K)$ ($\mu\Omega\cdot cm$) | $T_c$ (K) | $T^*$ (K) | $p(x; y)$ | $p(T_c; T_{c,max})$ | $\bar{p}$ |
|-------|----------------|----|----------------|----|------------------------------|---------|---------|-----------|-------------------|---------|
| #Pr1  | 240            | Pr: 20 | 1000        | 1.0 ± 0.05 | 311 | 61.2 | 92 ± 4 | (0.114 ± 0.005) | 0.100 ± 0.002 | 0.100 ± 0.005 |
| #Pr2  | 240            | Pr: 20 | 1000        | 1.0 ± 0.05 | 221 | 71.5 | 155 ± 5 | 0.114 ± 0.005 | 0.112 ± 0.002 | 0.112 ± 0.003 |
| #Pr3  | 324            | Pr: 10 | 1000        | 1.0 ± 0.05 | 73  | 86.3 | 130 ± 13 | 0.151 ± 0.01 | 0.145 ± 0.005 | 0.147 ± 0.008 |
| #Ox1  | 270            | 0      | 1           | 0.52 ± 0.03 | 348 | 56.0 | (255 ± 5) | 0.086 ± 0.006 | 0.093 ± 0.001 | 0.092 ± 0.002 |
| #Ox2  | 324            | 0      | 3.5         | 0.85 ± 0.05 | 162 | 87.0 | 208 ± 7 | 0.156 ± 0.01 | 0.140 ± 0.005 | 0.145 ± 0.008 |
| #Ox3  | 324            | 0      | 50          | 0.92 ± 0.05 | 119 | 89.8 | 155 ± 5 | 0.170 ± 0.01 | 0.160 ± 0.005 | 0.163 ± 0.008 |
| #Ox4  | 270            | 0      | 1000        | 1.0 ± 0.05 | 86  | 88.0 | 102 ± 3 | 0.187 ± 0.01 | 0.176 ± 0.005 | 0.180 ± 0.008 |
| #Ca1  | 324            | Ca: 5  | 1000        | 1.0 ± 0.05 | 60  | 85.0 | 133 ± 12 | (0.212 ± 0.01) | 0.186 ± 0.005 | 0.186 ± 0.01  |
| #Ca2  | 324            | Ca: 5  | 1000        | 1.0 ± 0.05 | 97  | 82.7 | 93 ± 1  | 0.212 ± 0.01 | 0.191 ± 0.005 | 0.198 ± 0.008 |

TABLE II. Analyses of the electronic responses and the self-energy effects of the $B_{1g}$ phonon at $T = 18 \, K$ of the $Y_{1-x}(Pr, Ca)_x Ba_2 Cu_3 O_{6+y}$ films and the single crystal. The energies $2\Delta(\sigma)$ represent the center frequencies of the peaks in the electronic responses in $\sigma$ symmetry ($2\Delta$ peaks). Also given are the exponents $z$ that describe the slopes $\omega^z$ of the electronic responses for $\omega \to 0$. The values $\Delta\omega_\nu$ and $\Delta\gamma_\rho$ describe the frequency shifts and broadenings relative to the anharmonic decay. They are given in brackets for the film #Pr1 in which a lattice distortion is observed around 150 K.

| Film  | $2\Delta(A_{1g})$ (cm$^{-1}$) | $2\Delta(B_{1g})$ (cm$^{-1}$) | $\omega^z(A_{1g})$ | $\omega^z(B_{1g})$ | $\Delta\omega_\nu$ (cm$^{-1}$) | $\Delta\gamma_\rho$ (cm$^{-1}$) |
|-------|-----------------------------|-----------------------------|-------------------|-------------------|-------------------------------|-------------------------------|
| #Pr1  | 270 ± 20                    | -                           | -                 | (-4.6)            | (-1.0)                        |                               |
| #Pr2  | 290 ± 20                    | -                           | 0.9               | 0.4               | -1.6                          | -2.5                          |
| #Pr3  | 325 ± 10 580 ± 10           | 1.2                         | 0.6               | -4.9              | -1.5                          |                               |
| #Ox1  | -                           | -                           | 0.2               | 0.3               | -0.3                          | -0.3                          |
| #Ox2  | 295 ± 10 540 ± 25           | 0.8                         | 0.4               | -3.5              | -0.8                          |                               |
| #Ox3  | 305 ± 10 515 ± 20           | 1.2                         | 0.9               | -5.6              | -0.5                          |                               |
| #Ox4  | 280 ± 20 390 ± 10           | 1.0                         | 1.0               | -6.7              | 5.3                           |                               |
| #Ca1  | 270 ± 20 350 ± 20           | 0.9                         | 0.5               | -4.0              | 3.1                           |                               |
| #Ca2  | 245 ± 20 305 ± 20           | 1.2                         | 1.7               | 0.8               | 5.4                           |                               |
| #sc   | 335 ± 15 435 ± 10           | 1.1                         | 1.0               | -8.6              | 1.9                           |                               |