Doping Dependence of the Electronic Interactions in Bi-2212 Cuprate Superconductors: Doped Antiferromagnets or Antiferromagnetic Fermi Liquids?

M. Rübhausen,* O. A. Hammerstein, A. Bock, and U. Merkt
Institut für Angewandte Physik und Zentrum für Mikrostrukturforschung, Universität Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany

C. T. Rieck
I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstraße 9, 20355 Hamburg, Germany

P. Guptasarma and D. G. Hinks
MSD-STCS, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

M. V. Klein
STCS, University of Illinois, 104 South Goodwin Avenue, Urbana, Illinois 61801
(Received 19 October 1998)

Electron-electron interactions in overdoped Bi-2212 are studied by inelastic light scattering. The optimally to slightly overdoped compounds exhibit two-magnon excitations with a dependence on the incident photon energy typical for doped antiferromagnets. For more overdoped samples, no two-magnon excitation is visible, indicating an antiferromagnetic correlation below twice the lattice parameter. In the same samples, the gap excitation shows a resonance similar to the two-magnon excitation. We interpret our results as a development towards a correlated Fermi liquid when the doping is increased. [S0031-9007(99)09467-3]

PACS numbers: 74.25.Gz, 74.72.Hs, 75.30.Et, 78.30.Hv

High-T_c cuprates have a rich phase diagram with regions of superconductivity close to the antiferromagnetic instability [1–3]. The common structural elements are copper-oxide planes surrounded by buffer layers for the doping of the planes. Strong experimental evidence exists that superconductivity is connected to the copper-oxide planes, which exhibit three-dimensional Néel ordering at temperatures between 300 and 500 K in the undoped case [1,4,5].

The fact that the maximum critical temperature of the cuprate superconductors occurs at low doping concentrations of roughly 0.16 holes per copper-oxide plane and unit cell, made it very tempting to consider the antiferromagnetic order as important for the mechanism causing superconductivity [1–3,6]. Since antiferromagnetic signals in the superconducting phases have been found in neutron scattering [7], nuclear magnetic resonance [8], and Raman scattering [9,10], there is certainly some support for these ideas. However, it has remained unclear just what the nature of this persisting antiferromagnetism is and how it can be properly accounted for. There are at least two different general approaches. First, one can consider cuprates as doped antiferromagnets [6]. In this framework the effective magnon-hole Hamiltonian has the same form as the Fröhlich interaction between electrons and phonons, leading to an attractive interaction between the holes resulting in critical temperatures of the order of 60 K and a d-wave-like order parameter. Second, one can assume that the properties of the cuprates are dominated by the holes and that the Coulomb on-site repulsion acts more as a perturbation. This leads, e.g., to a fluctuation-exchange (FLEX) approach to the Hubbard Hamiltonian or to the phenomenologically introduced spin-fluctuation interaction between the holes. The latter approaches are based on the concept of an antiferromagnetically correlated Fermi liquid and yield d-wave order parameters as well as relatively high critical temperatures [1–3]. A discrimination between these two general pictures can be achieved only by a simultaneous investigation of the electronic and magnetic properties of the cuprates. In particular, the investigation of the question, "How does a change in the magnetic properties affect the electronic properties?" gives direct information about their interplay.

Inelastic light scattering has given crucial information on the magnetic and electronic excitations [9–15]. Magnetic excitations have been studied from the undoped to the optimally doped regime and the evolution of the damping and the dispersion of the magnons with doping has been revealed [9,10,13,16]. The polarization dependence of the gap excitations in the superconducting state has shown unambiguously that the order parameter is anisotropic [17,18]. In the under to optimally doped compounds, the observation of an enhancement of the magnetic excitations occurring in conjunction with a suppression of electronic spectral weight below T_c, i.e., the rearrangement, has already provided information on the coupling between holes and magnons and shows that the magnon-hole interaction becomes modified in the superconducting state [10,19]. Most recently, we have shown that the reduction of spectral weight is related to the "dip-feature" observed in the electronic single-particle spectroscopies like angle-resolved photoemission spectroscopy (ARPES) or tunneling spectroscopy [19,20].

In this Letter we provide evidence that overdoped Bi-2212 cuprate superconductors exhibit an unexpected sudden change at high doping levels in the two-magnon response and the resonance properties of the pair-breaking excitation. This most likely indicates a transition from a doped antiferromagnet to an antiferromagnetically correlated Fermi liquid. Furthermore, as the two-magnon excitation vanishes in overdoped samples with critical temperatures as high as 76 K, we suggest that a purely magnon driven mechanism can be ruled out or is changing its nature at higher doping levels.

On a quasitetragonal lattice, Raman scattering allows access to four different scattering configurations, namely, B_{1g}, $A_{1g} + B_{2g}$, $A_{1g} + B_{1g}$, and B_{2g}. From the scattering occurring in the antiferromagnet and its doping dependence it is clear that the B_{1g} channel is dominated by the magnetic response, whereas the $A_{1g} + B_{2g}$ configuration shows electronic features similar to the ones obtained by tunneling spectroscopy and ARPES [19–21]. Therefore, magnetic excitations and their change with doping can be studied best in B_{1g} symmetry. All spectra displayed here are corrected for the thermal Bose factor and the spectral response of the spectrometer using a double-Ulbricht sphere system for the calibration of the setup. More experimental details can be found in Ref. [19]. The Bi-2212 samples have been carefully chosen with regard to sharp superconducting transitions. Surface contaminations can be avoided by freshly cleaving the compounds. The excellent homogeneity of the samples can be seen in, e.g., superconductor-insulator-normal tunneling measurements showing reproducible spectra over large regions of the sample surface. The critical temperatures are 95, 82, 76, and 72 K ($\Delta T_c \approx$ 1 K for all samples) and represent optimally to overdoped compounds. The data for the 95 K sample have been shown in Ref. [19].

Figure 1 depicts the B_{1g} response for three different overdoped compounds. The Raman response from 50 to 5500 cm^{-1} is displayed in Fig. 1(a). In (i) one observes an essentially flat background above the critical temperature and the appearance of peaks around 450 cm^{-1} and slightly above 2000 cm^{-1} in the superconducting state. The enhancement of scattering intensity around 2000 cm^{-1} below the critical temperature of the 82 K sample is part of the rearrangement and also observed in the B_{1g} data of the optimally doped 95 K sample. This behavior is similar in under and optimally doped Y-123 compounds [10]. The assignment of this peak at 14 K in B_{1g} symmetry to a two-magnon excitation is supported by doping dependent studies of Blumberg *et al.* on strongly underdoped up to optimally doped Bi-2212 [9]. The peak around 450 cm^{-1} is the gap excitation as displayed in more detail in Fig. 1(b). The spectrum (ii) in Fig. 1(a) exhibits a featureless high-energy background which does not change with temperature. The gap feature is clearly more pronounced and in contrast to the behavior of the 82 K sample in (i) the dominant superconductivity-induced effect. This sudden change is quite remarkable since the doping is only slightly altered leading to a change of T_c of only 6 K. Furthermore, there are no obvious two-magnon excitations visible anymore indicating that the antiferromagnetic correlation length has dropped below $2a$. The sample with a T_c of 72 K shown in Fig. 1(a) supports this observation. However, with overdoping a broad and weak feature around 3000 cm^{-1} seems to emerge, which is not affected by the superconducting transition.

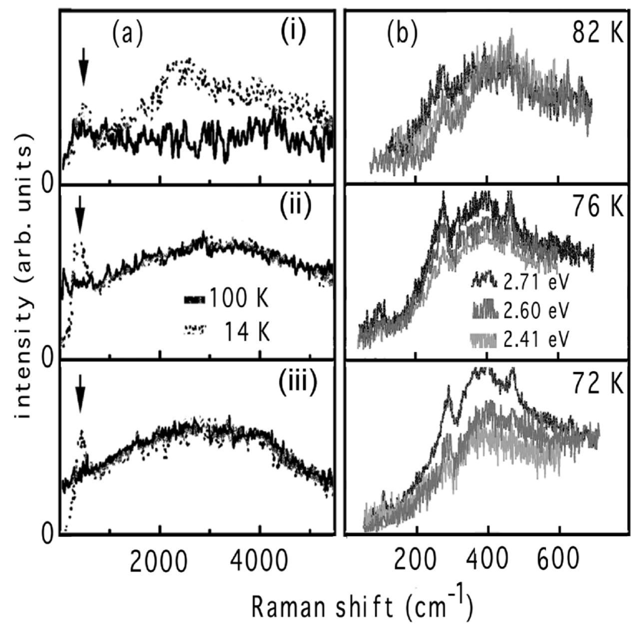

FIG. 1. Doping dependence of the Raman spectra in B_{1g} symmetry of overdoped Bi-2212 single crystals. In (a) we show the high-energy response taken with 2.71 eV at temperatures of 100 K (solid lines) and 14 K (dotted lines). The gap feature is marked by arrows. In (b) we have expanded the gap regime and show the resonance dependence of the gap feature on the incident photon energy. Incident photon energies (eV) and critical temperatures (K) are indicated.

Taking the peak positions of the gap from Fig. 1(b), we find that the gap shifts with doping towards smaller energies of 400 cm^{-1} and less in the 76 and 72 K compounds. In view of the gap of 500 cm^{-1} in the optimally doped 95 K sample [19], it seems that the gap excitation shifts with overdoping towards smaller excitation energies as previously reported on overdoped Bi-2212 as well as overdoped Tl-2201 [22,23]. This finding is also in agreement with tunneling data measured on similar Bi-2212 compounds [21]. In contrast to the 82 and 95 K samples the more overdoped 76 and 72 K samples show a clear enhancement of the gap intensity towards increasing incident photon energies. A similar behavior has been reported on overdoped Tl-2201 by Kang *et al.* [23], but not on optimally or slightly overdoped Bi-2212 by Opel *et al.* [24]. Our doping dependent measurements reveal the existence of two regimes. One group of samples, namely the lower doped ones, exhibit a nonresonant gap excitation and a two-magnon peak, whereas the stronger overdoped samples show a resonance in the gap feature and no two-magnon excitation.

In Fig. 2 we compare the resonance properties of the gap feature and the two-magnon peak by plotting the inverse integrated intensities versus the incident photon energy. The gap feature was integrated ± 100 cm^{-1} around the peak in order to avoid inclusion of phononic scattering being visible in the spectra. The two-magnon peak was integrated up to 4000 cm^{-1}. For comparison, the two integrals were normalized by their respective integration interval. Within the experimental error our results indicate that the gap features of the overdoped samples resonate at a similar energy as the two-magnon excitation in the under and optimally doped compounds. This provides strong evidence that the same intermediate state is responsible for the magnetic and electronic process.

In order to connect the resonance properties of the gap, the two-magnon peak, and their doping dependence on a microscopic level we present an interpretation based on a one-band Hubbard model. This allows us to consider electronic correlation effects. We are motivated by the validity of the Heisenberg model of antiferromagnetism (HAFM) in the undoped compounds and the concomitant appearance of electronic features and a two-magnon peak. Here, we do not attempt to make any quantitative estimates as this requires a commitment to one of many different representations of the Hubbard model.

At half filling the antiferromagnetic instability is governed by the ratio of the Coulomb on-site repulsion U to the hopping matrix element t. In the strong-coupling limit U is much larger than t, resulting in an effective spin picture. The matrix elements responsible for the spin Hamiltonian are of second order in t and describe the hopping of electrons to an adjacent site and back. A doubly occupied site is the intermediate state and has an energy of U. Thus, the energy scale of the spin excitations is set by the superexchange energy $J = 4t^2/U$. The coupling of light to these spin excitations occurs via the $\mathbf{P} \cdot \mathbf{A}$ part in the interaction of light with matter. The corresponding matrix elements are quadratic in the vector potential $\mathbf{A}$ of the light representing incident and scattered photons. Therefore, Raman scattering can probe directly the second-order matrix elements responsible for the superexchange as shown in Fig. 3. A projection of the states involved onto spin states leads to the HAFM and the interaction Hamiltonian of Fleury and Loudon with a peak position of the two-magnon peak of $\approx$3J due to 6 broken antiferromagnetic bonds as indicated in Fig. 3 [25]. A projection onto a spin state implies that the surrounding nearest-neighbor sites are spin aligned. This requirement is fulfilled at half filling. However, with increasing doping the number of spin vacancies increases leading to a breakdown of an effective spin picture when the nearest neighbor sites are empty. Hence, the critical antiferromagnetic correlation length to justify the application of a spin picture is $2a$, where a is the distance between two sites. For this second-order process, one expects a resonance enhancement, when the photon energy is of the order of U [26]. As shown in Fig. 3, this energy corresponds to the difference of the lower (LHB) and upper (UHB) Hubbard band, i.e., the difference between a doubly and singly occupied state. Resonances have been studied in many cuprates yielding resonance energies of

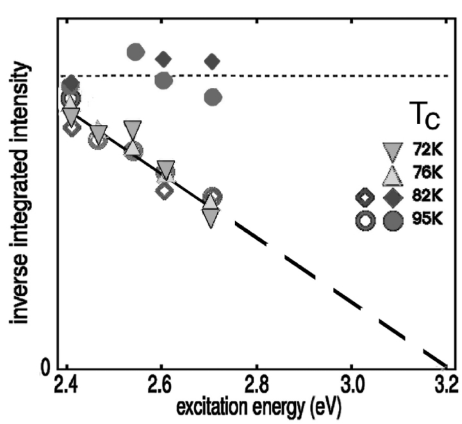

FIG. 2. Resonance enhancement of the gap excitation (closed symbols) and the two-magnon peak (open symbols) for various compounds as indicated. Lines serve as guides to the eye. The 95 K data are taken from Ref. [19].

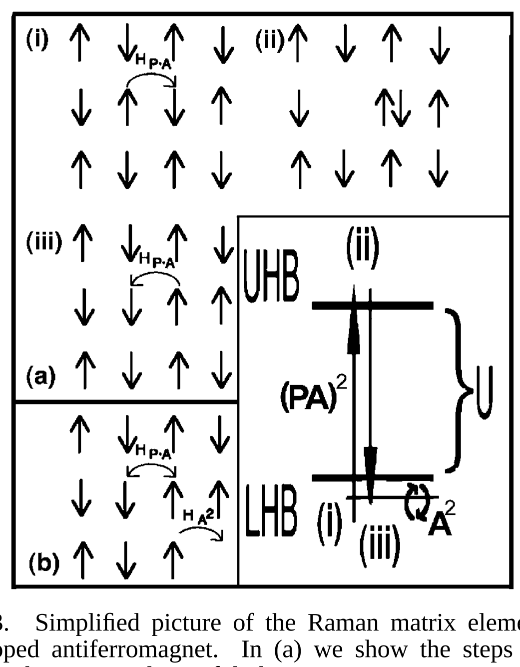

FIG. 3. Simplified picture of the Raman matrix elements in the doped antiferromagnet. In (a) we show the steps of the superexchange coupling of light to magnetic excitations. In (b) the effective superexchange spin flip coupling as shown in detail in (a) and charge coupling contributing away from half filling are depicted. The inset shows the action of both contributions in a band picture involving lower and upper Hubbard bands.

2.5 to 3.5 eV [9,27,28]. Since the superexchange energy J can be taken from the two-magnon peak and has been determined for all compounds to be $J \approx 0.1$ eV [9,27], we estimate a hopping matrix element $t \approx 0.27$ eV, so that Raman scattering indicates $t/U \approx 0.1$ at half filling. We note that the two-magnon excitation and its resonance property is therefore a direct consequence of a $(\mathbf{P} \cdot \mathbf{A})^2$ process within a nearest-neighbor spin environment.

Away from half filling it is important to know whether a strong coupling scenario still holds or not. Considering the discussion following Fig. 1, one finds that the two-magnon excitation broadens and shifts only slightly with increasing doping towards lower energies. Furthermore, it is evident from Fig. 2 that the resonance properties are hardly changed with doping. Therefore, the value of t/U remains small. In a strong coupling approach to the one-band Hubbard Hamiltonian, it can be shown that the effective Hamiltonian contains a spin part due to the second-order matrix element and a kinematic part [29]. Consequently, in addition to the $\mathbf{P} \cdot \mathbf{A}$ term one has to consider the coupling of light in first order via a nonresonant term proportional to $\mathbf{A}^2$ [10,26]. This leads to the matrix elements shown in Fig. 3(b). The double sided arrow indicates the $(\mathbf{P} \cdot \mathbf{A})^2$ coupling shown in detail in (a) competing with the $\mathbf{A}^2$ coupling, which is connected to the hopping of a single spin onto a spin vacancy as indicated by the single sided arrow in (b). In the inset, the small circle denotes the action of $\mathbf{A}^2$ in a band picture around the Fermi level (gray line). For small doping levels, all $\mathbf{P} \cdot \mathbf{A}$ transitions from the lower to the upper Hubbard band and back can be projected onto spin states. Hence for a doped antiferromagnet a resonant two-magnon feature still exists indicating the existence of a spin background together with a nonresonant gap excitation. Such a scenario would describe our observations from the 82 K sample in Fig. 1.

Increasing the doping to a level yielding an antiferromagnetic correlation length below $2a$ terminates any reasonable static spin picture. However, the spin environment might be partly restored leading to correlations between only two or three spins, so that a process involving a doubly occupied site is still possible, but cannot be reflected in a magnetic response, as the spin alignment of the final state no longer has dominant importance. Such a process would be reflected in a chargelike response exhibiting the same resonance energy as the two-magnon excitation. This scenario resembles a Fermi-liquid picture with a local exchange of U. Here, one would expect no two-magnon excitation but a resonant gap feature with a resonance energy close to the two-magnon resonance of the more antiferromagnetic compounds. The samples with a T_c of 72 and 76 K seem to be well described within such a Fermi-liquid-like picture.

In summary, we have provided experimental evidence that the persisting antiferromagnetic order qualitatively changes its behavior in the overdoped Bi-2212 compounds from a doped antiferromagnet to a scenario that is more in agreement with an antiferromagnetically correlated Fermi liquid in strongly overdoped compounds. Furthermore, as the two-magnon excitation disappears in overdoped samples with a T_c of still 76 K, we suggest that a purely magnon driven mechanism causing superconductivity can be ruled out or changes its nature at higher doping levels.

We acknowledge stimulating discussions with S. Ostertun, J. Bäckström, M. Käll, and L. Börjesson. This work was supported from the NSF through the STCS via DMR 91-20000, the DFG via the Graduiertenkolleg "Physik nanostrukturierter Festkörper" and Ru773/1-1, as well as the TFR via DOSS 251 DNR97-597.

*Present address: Loomis, 1110 W. Green St., Urbana, IL 61801.

[1] D. J. Scalapino, Phys. Rep. **250**, 329 (1995).
[2] P. W. Anderson, *The Theory of Superconductivity in High T_C Cuprates* (Princeton University Press, Princeton, NJ, 1997).
[3] D. Pines, Physica (Amsterdam) **282C–287C**, 273 (1997).
[4] N. P. Ong, *Physical Properties of High-Temperature Super Conductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Vol. 2, p. 459.
[5] A. Schilling *et al.*, Nature (London) **363**, 56 (1993).
[6] N. M. Plakida *et al.*, Phys. Rev. B **55**, 11 997 (1997).
[7] S. M. Hayden *et al.*, Phys. Rev. Lett. **76**, 1344 (1996).
[8] R. Stern *et al.*, Phys. Rev. B **52**, 15 734 (1995).
[9] G. Blumberg *et al.*, Science **276**, 1427 (1997).
[10] M. Rübhausen *et al.*, Phys. Rev. B **56**, 14 797 (1997).
[11] A. Yamanaka *et al.*, Jpn. J. Appl. Phys. **27**, 1902 (1988).
[12] R. Hackl *et al.*, Phys. Rev. B **38**, 7133 (1988).
[13] D. Reznik *et al.*, Phys. Rev. B **48**, 7624 (1993).
[14] K. B. Lyons *et al.*, Phys. Rev. Lett. **60**, 732 (1988).
[15] S. Tajima *et al.*, Phys. Rev. B **47**, 12 126 (1993).
[16] M. Pressl *et al.*, J. Raman Spectrosc. **27**, 343 (1996).
[17] M. V. Klein and S. B. Dierker, Phys. Rev. B **29**, 4976 (1984).
[18] T. P. Devereaux *et al.*, Phys. Rev. Lett. **72**, 396 (1994).
[19] M. Rübhausen *et al.*, Phys. Rev. B **58**, 3462 (1998).
[20] M. R. Norman *et al.*, Phys. Rev. Lett. **79**, 3506 (1997).
[21] Y. DeWilde *et al.*, Phys. Rev. Lett. **80**, 153 (1998).
[22] C. Kendziora *et al.*, Phys. Rev. Lett. **77**, 727 (1996).
[23] M. Kang *et al.*, Phys. Rev. Lett. **77**, 4434 (1996).
[24] M. Opel and R. Hackl (private communication).
[25] P. A. Fleury and R. Loudon, Phys. Rev. **166**, 514 (1968).
[26] B. S. Shastry and B. I. Shraiman, Phys. Rev. Lett. **65**, 1068 (1990).
[27] M. Rübhausen *et al.*, Phys. Rev. B **53**, 8619 (1996).
[28] W. Brenig *et al.*, Physica (Amsterdam) **237B–238B**, 95 (1996).
[29] A. B. Harris *et al.*, Phys. Rev. B **3**, 961 (1971).