

Evidence for a strong impact of the electron-photon matrix element on angle-resolved photoelectron spectra of layered cuprate compounds

S. Haffner, C. G. Olson, L. L. Miller, and D. W. Lynch

Department of Physics and Astronomy and Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011

(Received 26 January 2000)

Little is known about the impact of the electron-photon matrix element on angle-resolved photoelectron spectra of layered cuprate compounds. Using the example of the model layered cuprate $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, we demonstrate that the electron-photon matrix element has a significant influence on energy distribution curves, rendering their interpretation as images of the spectral function nontrivial.

Angle-resolved photoelectron spectroscopy (ARPES) has played an important role in the study of layered cuprate compounds such as, for example, the high-temperature superconductors. Examples of results obtained by ARPES are the existence of a Fermi surface in the normal state compatible with the Luttinger theorem¹⁻³ and the observation of the superconducting gap and its anisotropy as well as a gap in the normal state in the underdoped regime.⁴⁻⁶ One of the appealing features of ARPES is that the spectral intensity of an electron distribution curve (EDC) is directly proportional to the electron-photon matrix element weighted spectral function.⁷ Direct insight into the spectral function can therefore be gained, which currently is not possible with any other experimental method. ARPES also allows a direct comparison to theoretical models, as the spectral function is directly proportional to the imaginary part of the one-electron Green's function of many-body theory.⁸

Nonetheless, one has to stress that the spectral intensity observed in an EDC is proportional to the electron-photon matrix element weighted spectral function and not the spectral function itself. In most studies the influence of the matrix element on an EDC is ignored although calculations suggest that the relationship between ARPES intensities and the underlying electronic structure can be quite complicated due to matrix element effects, and that caution should be exercised in interpreting detailed features of the ARPES intensities in terms of the spectral function.⁹ In the following, using angle-resolved photoelectron spectra of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ as an example, it will be experimentally demonstrated that for layered cuprates the electron-photon matrix element can have a significant impact on both the relative spectral intensity and the shape of a feature in an ARPES spectrum.

Before discussing our results in detail, some information about $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ relevant for an understanding of this study is given. $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ was chosen as it can be regarded as a model system for the physics of layered cuprates having CuO_2 planes as their fundamental building block. $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is closely related to the undoped parent compounds of the high-temperature superconductors as it is also an antiferromagnetic insulator having a Néel temperature of 255 K.¹⁰ The CuO_2 planes in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are undoped (half filling); therefore the spectral intensity in an EDC related to the CuO_2 plane gives information about the dynamics of a single hole (the hole created by photoionization) in a CuO_2

plane. The ARPES experiments in this study were performed at 300 K. Although there is no long-range antiferromagnetic order at room temperature in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, the antiferromagnetic correlation length is still two orders of magnitude larger than the Cu-O distance.¹⁰ Therefore photoemission, as a fast and local probe, still registers the effect of antiferromagnetic order even 50 K above the Néel temperature.¹¹

The dynamics of a hole in a two-dimensional antiferromagnetic background is of fundamental interest itself and there have been numerous theoretical¹² and experimental^{11,13-16} studies of this subject. Of primary interest here are the lowest-lying states in an ARPES spectrum, the so-called first electron-removal states, which, according to most theoretical results, should be comprised of a low-binding-energy quasiparticle peak ascribed to the so-called Zhang-Rice singlet¹⁷ (ZRS) followed by incoherent spectral weight at higher binding energy due to quasiparticle dressing.¹² The first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ indeed show a well-developed low-binding-energy peak followed by additional spectral weight at higher binding energies for \mathbf{k} vectors along the Γ to (π, π) direction of the first Brillouin zone (BZ) of the CuO_2 plane.¹⁸ In this work we will not further elaborate on the physics behind the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ but rather use them for a study of the impact of the electron-photon matrix element on ARPES spectra of layered cuprates. They are well-suited models for this, since there are no complications due to apical oxygen atoms as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, no states derived from Cu-O chains as in $\text{YBa}_2\text{Cu}_3\text{O}_x$, no superstructure effects as in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BSCCO), and, finally, no Fermi energy cutoffs due to their insulating nature.

The angle-resolved photoelectron spectra were recorded on the storage ring Aladdin at the University of Wisconsin-Madison Synchrotron Radiation Center, on the Ames Laboratory/Montana State University ERG/SEYA beamline using a 50 mm radius hemispherical analyzer having a 2° full angular acceptance angle which corresponds to a \mathbf{k} resolution of 0.06 Å⁻¹ and 0.1 Å⁻¹ [5% and 9% of the distance between Γ and (π, π)] for the first electron-removal states and 22 eV and 35 eV photon energy, respectively. The total energy resolution was 105 meV and 115 meV for 22 eV and 35 eV photons, respectively. The angle of incidence of the photons was ~40° with respect to the sample surface normal. The $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ single crystal was grown as de-

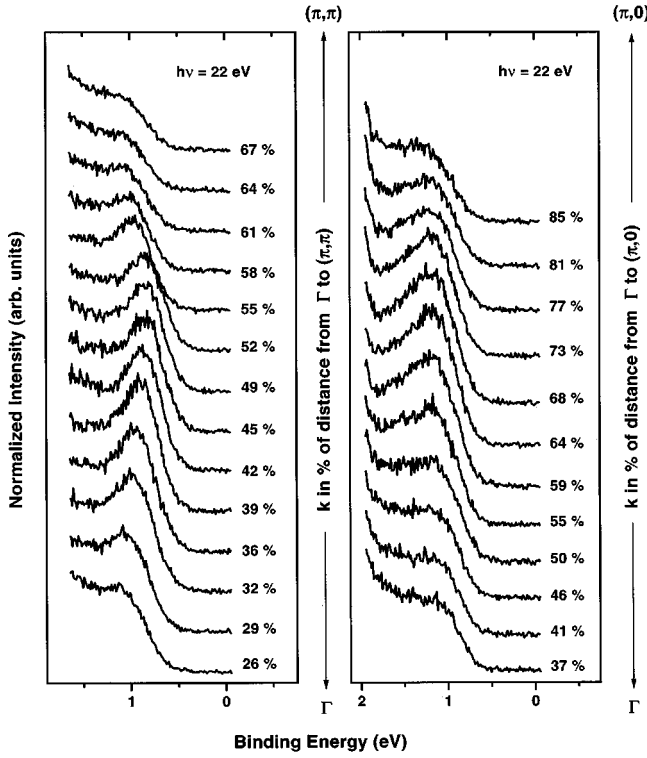


FIG. 1. $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ARPES spectra recorded along the Γ to (π, π) direction (left panel) and the Γ to $(\pi, 0)$ direction (right panel) of the first BZ using 22 eV photon energy. The \mathbf{k} vectors are given in % of the distance between Γ and $(\pi, \pi)/(\pi, 0)$.

scribed elsewhere.¹⁹ The sample was oriented *ex situ* by Laue backscattering and mounted with the Cu-O oxygen bonds in a horizontal/vertical plane. The sample was cleaved (cleavage plane parallel to CuO_2 planes) in the experimental chamber in a vacuum better than 6×10^{-11} Torr, and the sample alignment was confirmed *in situ* by using the symmetry of the dispersion of spectral features at high-symmetry points. All EDC's were recorded at room temperature and were normalized to the photon flux. The Fermi edge of a platinum foil in electrical contact with the sample was used as binding energy reference. There were no indications of charging effects because repeating an EDC for a \mathbf{k} point after the beam had decayed to less than half the current when the first EDC was taken gave the same EDC, except for signal strength. All ARPES spectra shown in this contribution were recorded within a time of 28 hours after the cleave of the sample and in one experimental run, i.e., using the same sample cleave. We observed no signs of sample degradation during this span of time.

Figure 1 presents the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for \mathbf{k} vectors along the Γ to (π, π) and the Γ to $(\pi, 0)$ directions in \mathbf{k} space recorded using 22 eV photon energy. For \mathbf{k} vectors from Γ to (π, π) we observe a distinct low-energy peak whose peak maximum has its lowest binding energy (~ 0.84 eV) at $\sim (\pi/2, \pi/2)$ and the majority of its spectral intensity for \mathbf{k} vectors before $(\pi/2, \pi/2)$. Along Γ to $(\pi, 0)$ there is a broad peak at ~ 1.1 - 1.2 eV binding energy, which can only be observed in a range of \mathbf{k} vectors from $\sim 50\%$ to $\sim 85\%$ of the distance between Γ and $(\pi, 0)$ and has its maximum spectral intensity at $\sim 70\%$ of the distance between Γ and $(\pi, 0)$. These results are in agreement

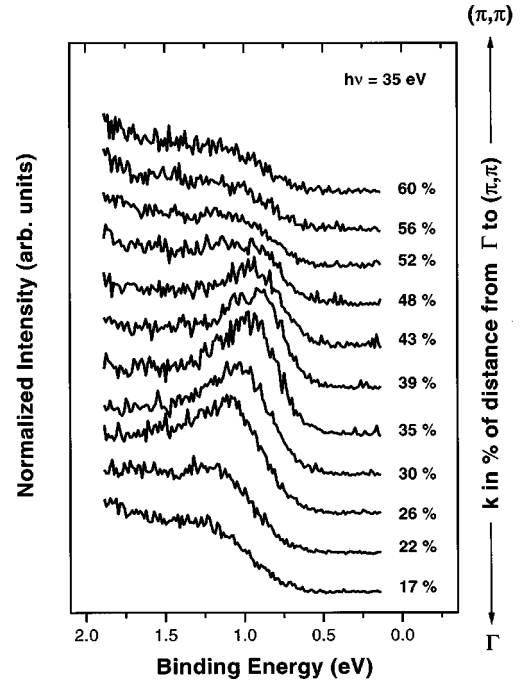


FIG. 2. $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ARPES spectra recorded along the Γ to (π, π) direction of the first BZ using 35 eV photon energy. The \mathbf{k} vectors are given in % of the distance between Γ and (π, π) .

with all previous studies of the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$,^{11,13} and the closely related $\text{Ca}_2\text{CuO}_2\text{Cl}_2$,^{14,15} which were recorded at about the same photon energy (22–25 eV) as the spectra shown in Fig. 1. This is no longer the case if we look at the first electron-removal states along Γ to (π, π) recorded using 35 eV photon energy, which are shown in Fig. 2. It is evident that there are differences between the 22 eV and the 35 eV Γ to (π, π) series of ARPES spectra, for example, in the relative strength of the peak as a function of \mathbf{k} . In Fig. 2 there is no well-developed peak at $(\pi/2, \pi/2)$ but only for \mathbf{k} vectors between $(0.26\pi, 0.26\pi)$ and $(0.43\pi, 0.43\pi)$, while in the left panel of Fig. 1 a distinct peak is observed from $(0.29\pi, 0.29\pi)$ up to $(0.58\pi, 0.58\pi)$. But, most notably, there are also differences in the line shape, which are reflected in the dispersion of the peak maxima presented in Fig. 3. While the dispersion relation deduced from the 22 eV data peaks at $\sim 50\%$ of the distance between Γ and (π, π) , the peak in the 35 eV data set has its minimum binding energy at $\sim (0.39\pi, 0.39\pi)$. From theory it is expected that the ZRS has its minimum binding energy along Γ to (π, π) at $(\pi/2, \pi/2)$.¹² In the following we will discuss possible reasons for the observed differences between the 22 eV and 35 eV ARPES data along the Γ to (π, π) direction in \mathbf{k} space and show that our $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ARPES data can be understood only in terms of a strong impact of matrix element effects on the EDC.

We can exclude the possibility that the observed differences are related to the sample or an extraordinary cleave of the sample, as our 35 eV data are recorded using the same sample and the same cleave as was used for the 22 eV data, which, as mentioned earlier, are in agreement with all previously published $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ARPES results recorded for 22–25 eV photon energy. This also excludes, besides our experimental precautions, the possibility of a misalignment

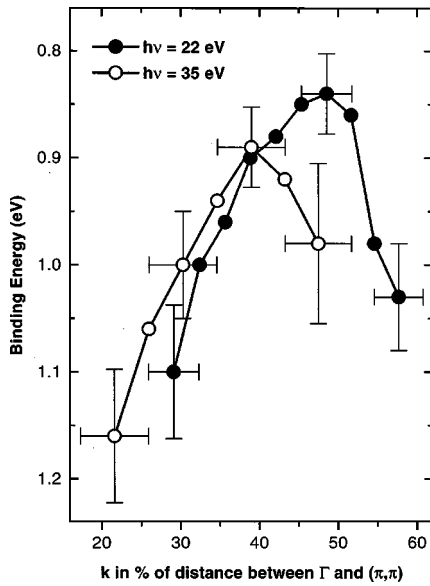


FIG. 3. Binding energy of the ZRS peak as a function of \mathbf{k} for \mathbf{k} vectors from Γ to (π, π) deduced from the spectra recorded at 22 eV (solid circles) and 35 eV (open circles) photon energy. Selected error bars are shown for reference.

of the sample. Charging can shift spectral intensity to higher binding energy and severely distort spectra, so one could argue that the fact that in the 35 eV ARPES spectra the peak maximum shifts back to higher binding energy before $(\pi/2, \pi/2)$ and also the lack of a distinct peak at \mathbf{k} vectors where one is observed in the 22 eV data are caused by charging. But note that the maximum photon flux during recording of the 35 eV ARPES spectra was still six times lower than the minimum photon flux during recording of the 22 eV ARPES spectra too, which is not the case.

From the foregoing discussion we can conclude that the spectra shown in Fig. 1 and in Fig. 2 truly represent the low-binding-energy ARPES response of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for 22 or 35 eV photon energy, respectively. Both Γ to (π, π) series of EDC's are equivalent in the sense that they show the lowest-lying excitations associated with the motion of a hole in an antiferromagnetically ordered CuO_2 plane for \mathbf{k} vectors along the Γ to (π, π) direction in the first BZ, i.e., the underlying spectral function is the same. The two series of EDC's differ, however, in the photoelectron momentum vector \mathbf{p} and the final state $|f\rangle$ and maybe also the initial state $|i\rangle$ (see the next paragraph) of the photoexcitation process, both factors that affect the electron-photon matrix element $\langle i|\mathbf{p} \cdot \mathbf{A}|f\rangle$ (where \mathbf{A} is the vector potential). As the underlying spectral function is the same in both cases, this suggests that the electron-photon matrix element is the reason for the observed differences.

The question remains how strongly the electron-photon matrix element influences the EDC's. One possibility is that we see different initial states dependent on, for example, photon energy but with the shape of the corresponding features in the ARPES spectra and their relative intensities as a function of \mathbf{k} being representative for the spectral function. In this case we have to explain the differences between the 22 eV and the 35 eV Γ to (π, π) spectra by assuming that the peak observed in the 22 eV spectra has a different physi-

cal origin from the peak observed in the 35 eV data. But, as mentioned earlier, up to now most authors have ascribed the peak evident in the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ or $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ to one excitation, the ZRS. It is also not possible that we observe only the coherent part of the spectral function of the ZRS for, for example, 22 eV and the incoherent part for 35 eV as both share a common matrix element. It has been suggested that a hole in an antiferromagnetically ordered Cu-O plane can decay into spinons and holons as is the case in one dimension.²⁰ But the spectral function predicted by the "two-dimensional spinon-holon model" does not show different peaks for the spinon and the holon, but only one peak due to an attractive spinon-holon interaction for \mathbf{k} vectors from Γ to (π, π) and a steplike feature for \mathbf{k} vectors from Γ to $(\pi, 0)$, in contradiction to the experimentally observed broad peak (see the right panel of Fig. 1). We have to conclude that according to current knowledge the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ have to be assigned to a ZRS, i.e., one initial state.

It should be evident now that there is no way to understand the differences between the 22 eV and 35 eV Γ to (π, π) ARPES spectra in the relative spectral intensities of the ZRS peak as a function of \mathbf{k} without at least assuming that the relative intensity of the ZRS peak in the spectra is strongly affected by the electron-photon matrix element. This is also in agreement with the previously mentioned theoretical results of Ref. 9 for the ARPES intensities of BSCCO. It remains to be clarified why the shape of the EDC's of the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is different for a given \mathbf{k} vector using 22 eV or 35 eV photon energy, which also leads to differences in the dispersion relations deduced from the spectra (Fig. 3).

Let us first discuss some possible reasons for this effect that would not be related to the electron-photon matrix element. First, it could be argued that the peak dispersion could be dependent on the momentum component perpendicular to the cleavage plane. But it should be emphasized that for a ZRS it is not expected that its dispersion will be dependent on the momentum component perpendicular to the CuO_2 planes (parallel to the cleavage plane).¹² Another reason could be the background as the ZRS peak is on top of a steplike feature which is also observed in the ARPES spectra of the high-temperature superconductors and whose origin is currently unknown. This steplike feature could influence the shape and the position of maximum intensity of the peak ascribed to the ZRS. But judging from spectra where there is no ZRS peak present, there seems not to be a lot of change of the shape of this background on going from Γ to (π, π) for the 22 eV or for the 35 eV data. The \mathbf{k} -dependent change of the location of the maximum of the ZRS peak should therefore not be influenced significantly by the background.

On the other hand, there is an explanation of the differences in line shape and dispersion of the $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ 22 eV and 35 eV ARPES spectra along Γ to (π, π) if one accepts that the electron-photon matrix element can influence the shape of an individual EDC. Note that both dispersion relations are equal within the error bars up to the \mathbf{k} vector after which the ZRS peak in the 35 eV ARPES spectra loses most of its intensity. It is only after this point in \mathbf{k} space that the dispersion relations deduced from the Γ to (π, π) 22 eV and 35 eV ARPES spectra differ. This suggests that the observed differences in line shape and dispersion are caused by the

electron-photon matrix element due to which the ZRS peak in the 35 eV ARPES spectra may be cut after $(0.39\pi, 0.39\pi)$, thus not only losing intensity but also having the maximum of the spectral intensity shifted to higher binding energy, leading to an apparent dispersion that is different from that of the ZRS peak in the spectral function. An influence of the electron-photon matrix element on the shape of an ARPES spectrum was not reported for the calculated BSSCO ARPES response of Ref. 9. A possible reason for this discrepancy could be the finite \mathbf{k} resolution of our ARPES experiment, which in conjunction with possibly significantly different dispersion relations of the final states reached using 22 eV and 35 eV photons could lead to a different shape of the 22 eV and 35 eV spectra for the same \mathbf{k} vector. Another reason could be that the calculations were performed in the framework of the local-density approximation, which is generally not well suited to describe either the lowest-lying occupied band of a layered cuprate or the final states 15 eV and more above the Fermi level.

In conclusion, we have observed that the electron-photon matrix element can have a profound impact on ARPES spectra of layered cuprates by significantly affecting the strength and the shape of spectral features. The results of this study clearly put emphasis on the need to apply the whole parameter range of the ARPES technique in order to get reliable, consistent, and complete information about the spectral function from an ARPES experiment. This is especially important when one has to rely on ARPES spectral intensities as is the case in an analysis of the momentum distribution function^{7,15} $n(\mathbf{k})$ (the momentum-integrated spectral intensity) and in the angle-scanning mode of angle-resolved photoelectron spectroscopy.²¹

The Ames Laboratory is operated by Iowa State University for the U.S. DOE under Contract No. W-7405-ENG-82. This work is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin, Madison, which is supported under Award No. DMR-95-31009.

-
- ¹C. G. Olson, R. Liu, D. W. Lynch, R. S. List, A. J. Arko, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Phys. Rev. B* **42**, 381 (1990).
- ²J. C. Campuzano, G. Jennings, M. Faiz, L. Beaulaigue, B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, and H. Claus, *Phys. Rev. Lett.* **64**, 2308 (1990).
- ³R. O. Anderson, R. Claessen, J. W. Allen, C. G. Olson, C. Janowitz, L. Z. Liu, J.-H. Park, M. B. Maple, Y. Daliachouch, M. C. de Andrade, R. F. Jardim, E. A. Early, S.-J. Oh, and W. P. Ellis, *Phys. Rev. Lett.* **70**, 3163 (1993).
- ⁴C. G. Olson, R. Liu, A.-B. Yang, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Science* **245**, 731 (1989).
- ⁵Z.-X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, A. G. Loeser, and C. H. Park, *Phys. Rev. Lett.* **70**, 1553 (1993).
- ⁶D. S. Marshall, D. S. Dessau, A. G. Loeser, C.-H. Park, A. Y. Matsuura, J. N. Eckstein, I. Bozovic, P. Fournier, A. Kapitulnik, W. E. Spicer, and Z.-X. Shen, *Phys. Rev. Lett.* **76**, 4841 (1996).
- ⁷M. Randeria, H. Ding, J.-C. Campuzano, A. Bellman, G. Jennings, T. Yokoya, T. Takahashi, H. Katayama-Yoshida, T. Mochiku, and K. Kadowaki, *Phys. Rev. Lett.* **74**, 4951 (1995).
- ⁸S. Huefner, *Photoelectron Spectroscopy* (Springer, Berlin, 1995).
- ⁹A. Bansil and M. Lindroos, *J. Phys. Chem. Solids* **59**, 1879 (1998).
- ¹⁰M. Greven, R. J. Birgeneau, Y. Endoh, M. A. Kastner, B. Keimer, M. Matsuda, G. Shirane, and T. R. Thurston, *Phys. Rev. Lett.* **72**, 1096 (1994).
- ¹¹B. O. Wells, Z.-X. Shen, A. Matsuura, D. M. King, M. A. Kastner, M. Greven, and R. J. Birgeneau, *Phys. Rev. Lett.* **74**, 964 (1995).
- ¹²E. Dagotto, *Rev. Mod. Phys.* **66**, 763 (1994).
- ¹³S. LaRosa, I. Vobornik, F. Zwick, H. Berger, M. Grioni, G. Margaritondo, R. J. Kelley, M. Onellion, and A. Chubukov, *Phys. Rev. B* **56**, R525 (1997).
- ¹⁴C. Kim, P. J. White, Z.-X. Shen, T. Tohyama, Y. Shibata, S. Maekawa, B. O. Wells, Y. J. Kim, R. J. Birgeneau, and M. A. Kastner, *Phys. Rev. Lett.* **80**, 4245 (1998).
- ¹⁵F. Ronning, C. Kim, D. L. Feng, D. S. Marshall, A. G. Loeser, L. L. Miller, J. N. Eckstein, I. Bozovic, and Z.-X. Shen, *Science* **282**, 2067 (1998).
- ¹⁶M. S. Golden, H. C. Schmelz, M. Knupfer, S. Haffner, G. Krabbes, J. Fink, V. Y. Yushankhai, H. Rosner, R. Hayn, A. Mueller, and G. Reichardt, *Phys. Rev. Lett.* **78**, 4107 (1997).
- ¹⁷F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
- ¹⁸ \mathbf{k} vectors are given in units of the inverse lattice constant of the CuO_2 plane.
- ¹⁹L. L. Miller, X. L. Wang, S. X. Wang, C. Stassis, D. C. Johnston, J. Faber, Jr., and C.-K. Loong, *Phys. Rev. B* **41**, 1921 (1990).
- ²⁰R. B. Laughlin, *J. Phys. Chem. Solids* **56**, 1627 (1995); *Phys. Rev. Lett.* **79**, 1726 (1997).
- ²¹P. Aebi, J. Osterwalder, R. Fasel, D. Naumovic, and L. Schlapbach, *Surf. Sci.* **307-309**, 917 (1994).