

## Anomalous Transfer of Spectral Weight in Doped Strongly Correlated Systems

H. Eskes, M. B. J. Meinders, and G. A. Sawatzky

*Materials Science Centre, Department of Solid State and Applied Physics, University of Groningen, Nijenborgh 18, 9747 AG Groningen, The Netherlands*

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A qualitative and quantitative description (exact diagonalization of finite clusters) of the doping dependence of one-electron-removal and -addition spectral weights is given. A half-filled Hubbard system in the localized limit has two low-energy electron-addition (-removal) states for each hole (electron) created by doping. In contrast, a charge-transfer system in the localized limit is fundamentally asymmetric between hole and electron doping. However, when the hybridization is increased this asymmetry disappears quickly and both holes and electrons introduced by doping show a strongly correlated behavior.

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A surprising feature of the high- $T_c$  materials is a strong doping dependence of high-energy spectral distributions, and a shift of spectral intensity from high to low energies. Two of the nicest examples are the electron-energy-loss study [1] and O 1s x-ray-absorption study [2] of the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system. These spectra show a strong decrease with  $x$  in the intensity of the upper Hubbard band as the lower-energy structure develops due to holes in the O 2p band. Such behavior has previously been found in Li-doped NiO as well [3].

Also, in optical-absorption experiments [4], a transfer of spectral weight from the band-gap transition at about 2 eV in insulating  $\text{La}_2\text{CuO}_4$  to the low-energy scale ( $< 1.0$  eV) in the superconductor  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  is observed. The integral of the optical conductivity up to 1 eV increases much more rapidly than the doping concentration would suggest. At the same time the high-energy-scale structure around 2 eV decreases rapidly, whereas the total integrated spectral weight up to 4 eV remains nearly constant. Similar behavior has also been found recently for the electron-doped system  $\text{Pr}_{2-x}\text{Ce}_x\text{O}_{4-\delta}$  by Cooper *et al.* [5].

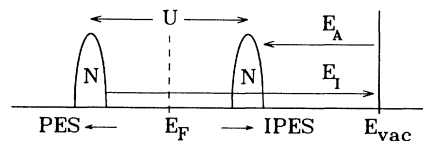
That these kinds of effects can be related to strong correlations is evidenced by exact diagonalization studies. A convincing description of the O 1s spectra is given using the Mott-Hubbard (MH) model [2]. Also, the calculated optical spectra for the MH and  $t$ - $J$  models show features quantitatively similar to what is seen experimentally [6-9].

At first glance one would not expect to see such spectral-weight transfers in the hole-doped high- $T_c$  materials, which are generally accepted to be charge-transfer (CT) systems, because the additional holes mainly occupy oxygen 2p states. In a previous paper [10] we found, however, using a multiband cluster ( $\text{Cu}_2\text{O}_7$ ) calculation and parameters suitable for the high- $T_c$  compounds and for 50% doping, a substantial transfer of spectral weight. In this paper we describe the physical origin of the observed spectral-weight transfer and its doping dependence. In addition we study both the MH and CT systems and describe the effects of hybridization. Special attention is

paid to the asymmetry in electron- and hole-doped systems expected in a CT model. We show that if the hybridization in a CT system is large enough, the spectral-weight transfer becomes similar to that of a MH model, but the physical origin is really quite different.

There is a simple picture which can be used to at least qualitatively understand the large spectral-weight readjustments in MH systems. Consider a row of  $N$  widely separated H atoms with one electron per atom in the ground state. The total electron-removal (photoelectron) and electron-addition (inverse photoelectron) spectral weight, shown in Fig. 1(a), is equal to the number of occupied and empty levels, respectively. Thus each has an intensity equal to  $N$ . Let us now consider a hole-doped chain of H atoms. There are now  $N-1$  singly occupied sites so we have  $N-1$  ways of removing an electron. At the same time there are  $N-1$  (not  $N$ ) ways of occupying the upper Hubbard band. This leaves two states at the site with the missing electron. Both of these are elec-

(a) Mott-Hubbard : Insulating



(b) Charge Transfer : Insulating

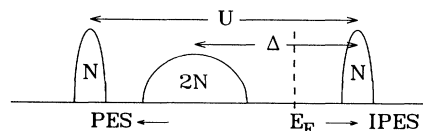


FIG. 1. A schematic drawing of the electron-addition and electron-removal spectra for the insulating undoped (a) Hubbard model and (b) charge-transfer model. The ionization potential  $E_I$  and electron affinity  $E_A$  are indicated, as well as the Hubbard repulsion  $U$  and charge-transfer energy  $\Delta = \epsilon_p - \epsilon_d$ .

tron-addition states (one with spin up and one with spin down), and they both have an energy corresponding to the lower Hubbard band. Therefore the Fermi level must lie at the position shown in the inset on the left of Fig. 2. This shows that the electron-addition spectral weight in the low-energy-scale part (around  $E_F$ ) goes as  $\alpha x$ , where  $\alpha=2$  and  $x$  is the doping concentration. One of these states comes from the upper Hubbard band so indeed there is a transfer of spectral weight from high to low energy [11]. The same arguments hold also for the electron-doped chain. This behavior is contrasted by one-electron systems where the spectral weight of bands is not influenced by doping. *A correlated system behaves quite differently from a semiconductor with respect to doping.*

In the high- $T_c$  superconductors, holes introduced by doping are known to be of mainly oxygen character and thus these materials have to be described as (doped) CT systems rather than MH systems [12]. In Fig. 1(b) a sketch of the electronic structure of a charge-transfer gap material is shown. There now exists, for the undoped material, a filled band of states between the lower Hubbard band and the Fermi level. A textbook example would be a chain of alternating H and Xe atoms. In the high- $T_c$  materials the role of H is played by  $\text{Cu}^{2+}$  (single occupied  $d_{x^2-y^2}$  state) and that of Xe by  $\text{O}^{2-}$  (filled  $2p$  band). In the localized limit, neglecting hybridization, hole doping will cause the Fermi level to move into the O

$2p$  band. Introducing a hole by doping will leave only *one* electron-addition state near the Fermi level while the upper Hubbard band retains  $N$  states. Thus this situation resembles a semiconductor. On the other hand, introducing electrons up to a concentration  $x$  yields  $2x$  electron-removal states at  $E_F$ , as in the MH case. So, in a CT system there is a fundamental asymmetry between hole and electron doping and for strongly ionic CT systems we would expect negligible transfer of spectral weight in the case of hole doping. This is in contrast to what is found for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [1,2]. The question arises in what respect strong hybridization changes this picture.

In order to study this we calculated first the one-particle Green's function obtained by exact diagonalization of finite clusters for the MH model, for different values of  $U/t$ . Details concerning the calculational techniques can, for instance, be found in Refs. [7] and [8]. The procedure is the following. Given a doping percentage  $x$  we calculate numerically the trace (over  $k$  and spin) of the electron-removal (-addition) Green's function. Then the gap energy  $E_{\text{gap}}$  (chosen to be the middle between the upper and lower Hubbard bands) is determined by inspection, and the partial integration up to  $E_{\text{gap}}$ , giving  $\alpha$ , is evaluated. The results for a periodic eight-site one-dimensional cluster are shown in Fig. 2. We have repeated the calculations for a two-dimensional  $3 \times 3$  site cluster. The results were found to be practically equivalent to the results shown in Fig. 2, as long as the bandwidth is kept constant. This suggests that the results are not very sensitive to low-energy characteristics, like the size and the dimensionality of the cluster, or the amount of frustration in the spin lattice. Instead the result is mainly determined by local factors like the parameter  $U/t$  and the number of nearest neighbors of a given site.

From the figure it is seen that the spectral weight grows, in fact, faster than twice the amount of doping and that this ratio is increasing as the value of  $U/t$  is decreased. The reason for this is the hybridization between low-energy electron-addition states and the upper Hubbard band. For  $U/t = -5$  ( $-10$ ) the line through the points corresponding to half-filling and the one-hole-doped case has a slope of 3.3 (2.5). The smallest cluster in which such an enhanced weight transfer can be seen contains only two sites. This cluster is easily solved by hand, giving a factor  $\alpha$  (for 50% doping) which ranges from 2 ( $U/t \rightarrow \infty$ ) to 2.5 ( $U/t \rightarrow 0$ ). For larger clusters and small values of  $U/t$  it becomes difficult to distinguish whether states belong to the upper or lower Hubbard band. Thus in order to have a sensible definition of  $E_{\text{gap}}$  we focused on large values of  $U/t$ . As  $U \rightarrow 0$  one returns to the one-free-particle band with no spectral-weight transfer.

For the CT model in the localized limit we have seen that upon hole doping the weight of the O band grows as the doping  $x$  and that the upper Hubbard band is not influenced. However, upon switching on the hybridiza-

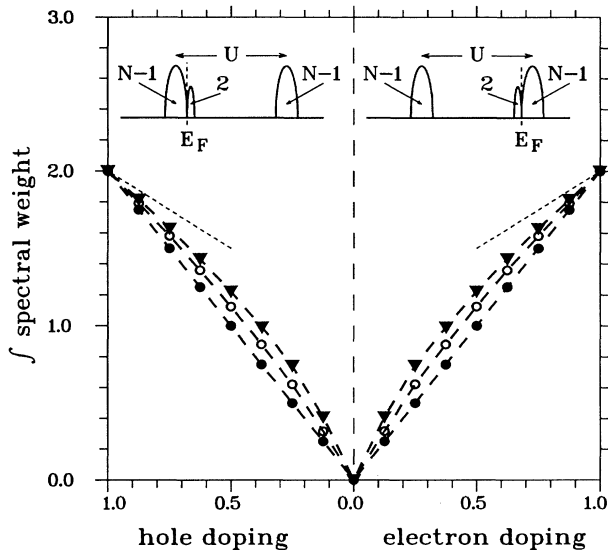


FIG. 2. The integrated low-energy spectral weight divided by the number of sites as a function of doping for the  $N=8$  site one-dimensional Hubbard chain with periodic boundary conditions. The curves correspond to the following:  $\bullet$ ,  $U/t \rightarrow \infty$ ;  $\circ$ ,  $U/t = -10$ ; and  $\blacktriangledown$ ,  $U/t = -5$ . The dotted line represents the free-particle limit. Inset: The intensities, shown schematically, of the electron-addition and -removal spectra for the Hubbard system with one additional hole (left) and one additional electron (right) in the localized limit.

tion the upper Hubbard band and the O 2*p* hole states start hybridizing in such a way that the phases of the wave function will constructively interfere for transitions to the low-energy-scale and destructively interfere for transitions to the high-energy-scale electron-addition states [10]. This causes transfer of spectral weight from the high- to the low-energy scale even though the number of states is unchanged. The low-energy-scale spectral weight can thus be expected to be  $\alpha x$ , with  $\alpha \geq 1$ . This is related to the well-known phenomenon that satellite intensities in spectroscopies in general decrease when the hybridization is increased.

For the high- $T_c$  materials it was proposed that the hole-doped systems can be described by a  $t$ - $J$  model [13] or a single-band Hubbard model [14]. Because in the  $t$ - $J$  model the occupation is constrained to at most one electron per orbital, it is easily checked that the low-energy spectral weight is equal to  $2x$ , so it behaves as a MH system in the localized limit. This means that the hybridization should strongly influence the character of the oxygen states near the insulating gap, resulting in a factor  $\alpha = 2$  if the  $t$ - $J$  model is valid.

The effect of the hybridization is studied by considering a one-dimensional periodic cluster with four unit cells. Each unit cell consists of two orbitals “*d*” and “*p*,” where “*d*” stands for the correlated atom and “*p*” for the free-electron (ligand) atom. The CT Hamiltonian used here contains on-site energies  $\epsilon_d$  and  $\epsilon_p$ , intersite hopping ( $t_{pd}$ ), oxygen bandwidth ( $t_{pp}$ ), and copper on-site repulsion ( $U_{dd}$ ). It can be shown that the cluster used here is equivalent to a  $\text{Cu}_4\text{O}_8$  cluster with periodic boundary conditions. This cluster was studied before [7,15,16] as representing the  $\text{CuO}_2$  planes of the high- $T_c$  superconductors.

The partial-sum-rule results are shown in Fig. 3 for different values of  $t_{pd}$ . In the case of electron doping the situation closely resembles the MH situation (Fig. 2). For hole doping the situation is quite different. For small values of the hopping  $t_{pd}$  the low-energy spectral weight follows the doping percentage, as argued before. When the value of  $t_{pd}$  is increased this spectral weight is seen to increase rapidly.

The role of  $t_{pp}$  is found to be small. If one increases  $t_{pp}$  the integral also increases, but only very slightly. This can probably be understood as a competition between the increasing *p* bandwidth and a decreasing effective value of  $\Delta = \epsilon_p - \epsilon_d$ . We also investigated what happens if one of the Hubbard bands is energetically far away. For the limit that  $U \rightarrow \infty$  and  $\Delta = 4$ , and with one additional hole, the integrated low-energy spectral weight  $\alpha = 1.54$ . The limit  $\Delta \rightarrow \infty$  and  $U = \Delta + 4$  gives  $\alpha = 1.24$ . Thus in both cases the value is strongly reduced as compared to the value 2.26 for  $U = 8$  (Fig. 3). This shows that both the upper and lower Hubbard bands are essential in order to get such strong transfers of spectral weight.

Because for the high- $T_c$  superconductors the transfer

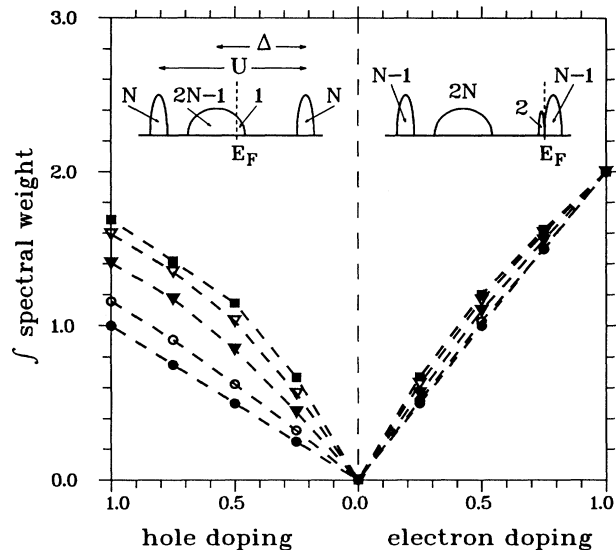


FIG. 3. The integrated low-energy spectral weight divided by the number of unit cells as a function of the doping for the  $N=4$  unit-cell charge-transfer system with periodic boundary conditions. The curves correspond to the following:  $\bullet$ ,  $t_{pd}=0$ ;  $\circ$ ,  $t_{pd}=0.5$ ;  $\blacktriangledown$ ,  $t_{pd}=1.0$ ;  $\triangledown$ ,  $t_{pd}=1.5$ ; and  $\blacksquare$ ,  $t_{pd}=2.0$  eV. For all curves,  $\epsilon_p - \epsilon_d = 4$ ,  $U_{dd} = 8$ , and  $t_{pp} = -0.25$  eV. Inset: The intensities, shown schematically, of the electron-addition and -removal spectra for the system with one additional hole (left) and one additional electron (right) in the localized limit.

integral  $t_{pd}$  is known to be large, these materials lie in the regime corresponding to the upper curves in Fig. 3 (solid squares). Therefore, the low-energy integrated spectral weight for hole doping is almost as large as the value for electron doping and the holes show a strongly correlated behavior. The use of the  $t$ - $J$  model also suggests such a symmetry between electron and hole doping. As shown previously [10], large hybridization is necessary to stabilize the Zhang-Rice singlet and to justify the reduction of the CT model to the one-band  $t$ - $J$  model. Using the Hubbard bands and the *p* band as an energy reference, the Fermi level is seen to shift into the *p* band or the upper Hubbard band when adding one hole or one electron, respectively. Thus we do not see indications that the Fermi level is fixed to the center of the insulating gap, as photoemission experiments on the high- $T_c$  materials seem to suggest [17]. However, we do see states appearing in the CT gap close to the Fermi level for hole as well as for electron doping.

In conclusion, we have shown that a transfer of spectral weight is in fact a general feature of strongly correlated systems. For the MH system a low-energy spectral weight growing as  $2x$ , where  $x$  is the percentage of holes from half filling, and at the same time a corresponding decrease of the upper-Hubbard-band spectral weight can be understood by counting the possibilities for adding an electron. The factor 2 was found to increase to an even

higher value when the intersite hybridization is taken into account. This transfer of spectral weight can be considered as a fingerprint of strongly correlated (mixed valence) systems.

In the limit of large  $U$  and small doping the MH model can be replaced by a  $t$ - $J$  model, with  $J=4t^2/U$ . Because of the restriction of at most single occupancy, the spectral weight should increase as  $2x$ . The MH model at low doping yields a value higher than 2 for  $U/t$  still in the large- $U$  regime, which is caused by virtual excitations to the upper Hubbard band. This gives a measure of the deviation from the  $t$ - $J$  model.

A CT system in the localized limit is fundamentally asymmetric in electron and hole doping. Electrons will feel the strong repulsions on the  $d$  sites, similar to the MH model, and will behave as strongly correlated objects. Holes, however, are in zeroth order free particles. A small hopping term will cause these holes to be scattered by the spin background, resulting in a situation comparable to the Kondo problem. Increasing the hopping changes this picture radically. Now the filled lower Hubbard band will hybridize with the  $p$  states, causing a sort of mirror lower Hubbard band to appear at the low-energy side of the  $p$  band, and the  $d$  spectral weight is strongly enhanced. The holes in this band will behave as correlated particles with restrictions on double occupancy. As a result, the spectral weight was shown to grow as fast as  $2x$  (or even faster), restoring, as far as this transfer of spectral weight is concerned, the symmetry between electrons and holes, and both behave as strongly correlated particles. This result is closely related to the way Zhang and Rice arrived at a  $t$ - $J$  model starting from the three-band model for the high- $T_c$  compounds. In our opinion, however, it is not clear if the hole- and electron-doped systems can both be described by a single Hubbard Hamiltonian. Because the holes are mainly on the  $p$  orbitals their motion will depend differently on parameters such as  $t_{pd}$  and  $t_{pp}$  than the motion of the electrons. Therefore if the hole-doped case could be described by such a one-band Hubbard approach, the parameters  $U$  and  $t$  could still be quite different from those for electrons.

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