Low Frequency Spectroscopy of the Correlated Metallic System $Ca_xSr_{1-x}VO_3$

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We study the photoemission and optical conductivity response of the strongly correlated metallic system $Ca_xSr_{1-x}VO_3$. We find that the basic features of the transfer of spectral weight in photoemission experiments and the unusual line shape of the optical response can be understood by modeling the system with a one-band Hubbard model close to the Mott-Hubbard transition. We present a detailed comparison between the low frequency experimental data and the corresponding theoretical predictions obtained within the local impurity self-consistent approximation that is exact in the limit of large lattice connectivity. [S0031-9007(96)00327-4]

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The understanding of the redistributions of the spectral weight that occurs in strongly correlated systems is a fascinating problem of condensed matter physics [1–3].

Most transition-metal oxides have narrow conduction bands originated in partially filled $3d$ orbitals where correlation effects are significantly relevant. One of the classical examples is the V_2O_3 compound and its derivatives which exhibit a Mott transition, that is, a metal-insulator transition (MIT) driven by electronic correlations in the absence of magnetic ordering [4,5]. In a recent paper Fujimori *et al.* [6] examined the photoemission spectra of several transition-metal oxides, demonstrating the dramatic redistribution of spectral weight as a consequence of electronic correlations in those compounds.

Here, we consider another correlated system, $Ca_xSr_{1-x}VO_3$, which displays a notable transfer of weight as a function of x in its photoemission spectra [7,8], and very unusual features in the distribution of its low frequency optical response. This system is particularly interesting as it allows for *a systematic study* of the evolution of the spectral line shapes with x. We shall argue that the basic features observed in a recent photoemission study [7,8], and in the new optical conductivity results that are reported here, can be explained in terms of the solution of a single-band Hubbard model close to the MIT. We shall present a detailed comparison between the experimental data and the theoretical predictions of the model treated within the local impurity self-consistent approximation (LISA) which is exact in the limit of large connectivity, or, equivalently, large dimensionality [9–11].

The $Ca_xSr_{1-x}VO_3$ compound has a perovskite-type structure where the nominal valency of vanadium ions is 4+, which leaves only one $3d$ electron per vanadium ion in the conduction band. Thus, in a first approximation, we shall assume that the system can be modeled by a half-filled single-band Hubbard Hamiltonian. The hope is that this simple model may capture the basic features of the low energy physics that is experimentally observed.

The Hamiltonian of the Hubbard model reads

$$H = -\sum_{<i,j>}(t_{ij} + \mu)c_{i\sigma}^{\dagger}c_{j\sigma} + U\sum_i\left(n_{i\uparrow} - \frac{1}{2}\right)\left(n_{i\downarrow} - \frac{1}{2}\right), \qquad (1)$$

where summation over repeated spin indices is assumed.

The LISA method [10] is a dynamical mean field theory that is exact in the limit $q \to \infty$, where q is the connectivity of the lattice. Consequently, the hopping amplitude is rescaled as $t_{ij} \to \frac{t}{\sqrt{q}}$ to obtain a nontrivial model [9]. The lattice Hamiltonian is then mapped onto an equivalent impurity problem which is supplemented by a self-consistency condition. The detailed derivation of the resulting mean field equations is already given in great detail elsewhere [10–12]. We shall assume a semicircular bare density of states $\rho^0(\epsilon) = (2/\pi D)\sqrt{1-(\epsilon/D)^2}$, with $t = \frac{D}{2}$, which is realized in a Bethe lattice and on a fully connected, fully frustrated version of the model [13–15]. This density of states has the same edge behavior as one obtained from a three-dimensional tight-binding model. As there is only one $3d$ electron in the $Ca_xSr_{1-x}VO_3$ system, we set $\mu = 0$ which renders the model half filled. We use the second-order perturbative calculation (IPT) to iteratively solve the associated impurity problem [13]. It has already been shown elsewhere that this method is in excellent agreement with the exact solutions that can be obtained using exact diagonalization or quantum Monte Carlo techniques [10]. Still, we use the IPT calculation since the exact methods either lack the resolution or cannot reach the low temperature limit that is relevant for the present discussion.

The solution of the Hubbard model in the limit of large dimensions has been obtained recently [16]. One of the basic results is the existence of a MIT at an intermediate value of the interaction $U_c \approx 3D$ ($U_c = 3.37D$ within IPT). As the transition is approached by increasing U/D, one finds that the density of states

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splits into a characteristic three-peak structure. There is a central quasiparticle peak at the Fermi energy of width ϵ_F^* that narrows as the transition is approached, indicating the enhancement of the effective mass. This feature is accompanied by the incoherent lower and upper Hubbard bands that emerge at frequencies of the order of $\pm\frac{U}{2}$, and which acquire the spectral weight that is transferred from the lower frequencies as the central peak narrows [11,13].

From the theoretical standpoint, the $Ca_xSr_{1-x}VO_3$ compound is extremely interesting, since the chemical substitution of a Sr^{2+} ion by Ca^{2+} of the same valence modifies the V-O-V bond angle from $\sim 180^\circ$ to 160°, thus controlling the strength of the ratio U/D. Therefore, for concentrations ranging from $x = 0$ to 1, we go from a less correlated to a strongly correlated metal.

We now turn to the comparison between the experimental data and the theoretical predictions of the model Hamiltonian. The strategy will be to extract the relevant model parameters, i.e., U and D, from the experimental data, and use them as sole input for the theoretical model. We emphasize that, following this procedure, there are no free parameters left to adjust in the theoretical fit of the experimental data.

We first consider the recent experimental photoemission data of Inoue *et al.* [7] which we reproduce in Fig. 1. The low energy photoemission spectra consist of two contributions: a broad feature at higher frequencies and another one, much smaller and narrow, that occurs at the Fermi energy. As we increase the value of x, i.e., the correlation strength, we observe a systematic transfer of spectral weight between the two spectral features [7]. The line shape of this spectrum is very reminiscent of the results for the density of states that are obtained from the large dimensional approach to the Hubbard model close to the MIT point (see inset of Fig. 1). Thus, we associate the higher frequency feature to the lower Hubbard band (LHB) and the feature at the Fermi level to the low frequency quasiparticle contribution. We extract the model parameters noting that (i) the LHB features peak at approximately $-\frac{U}{2}$; (ii) the half-width of the LHB should approximately correspond to D; and (iii) the ratio of the quasiparticle peak to the LHB spectral weight is controlled by the ratio U/D in our model.

Photoemission experiments probe the occupied part of the density of states. Accordingly, we have multiplied the theoretical spectrum by the Fermi distribution function of 80 K, and then convoluted with a Gaussian function of width 0.3 eV that corresponds to the finite experimental resolution [7]. In Fig. 1 we display the results for the theoretical photoemission intensity. The estimated values for U and D are shown in the figure. We have checked that a good fit can also be obtained by a small variation of the parameters. Although one expects that D would also systematically change with composition, we choose to set equal to constant 1 eV. This choice not only provides a reasonable fit, but it further allows one to clearly appreciate the systematic evolution of the model line shape as a function of the interaction.

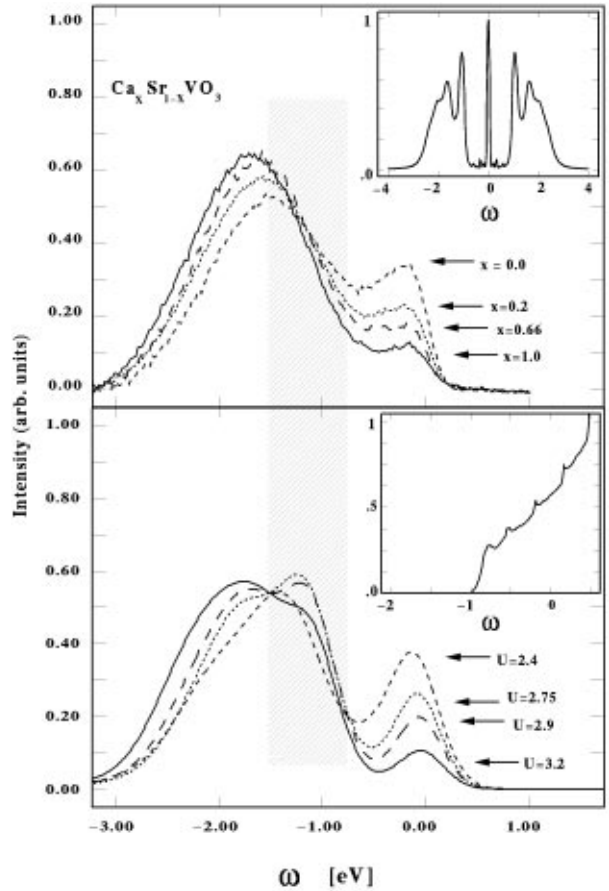

FIG. 1. Above: Experimental photoemission spectrum of $Ca_xSr_{1-x}VO_3$ at 80 K (from [7] with background from oxygen $2p$ band subtracted). The inset contains the theoretical density of states $\rho(\omega)$ obtained from IPT at $T = 0$ for a value of the interaction $\frac{U}{D} = 3$ close to the MIT. Below: Theoretical density of states $\rho(\omega)$ for the model parameter U indicated in the figure and $D = 1$ eV obtained by IPT. The data correspond to the $\omega < 0$ part of $\rho(\omega)$ convoluted with the experimental resolution. The inset shows the corresponding LDA results (from [7]).

It is apparent that the theory can successfully capture the basic features of the experimental data. We observe the transfer of spectral weight between the LHB and the quasiparticle peak as a function of the interaction. In particular, we note that the theory captures correctly the intermediate frequency range around which the transfer of weight occurs (indicated with a shaded region in the figure). These results are more remarkable in regard to the complete failure of the LDA method to capture even the most basic features of the data (inset Fig. 1) [7].

Although we find that the basic features of the transfer of spectral weight are very well captured by our model, upon a more detailed comparison one notes that some discrepancies remain, especially in regard to the shape of the

small quasiparticle peak and the lower energy edge of the LHB. The discrepancies in the shape of the quasiparticle contribution, in particular, the renormalization of the value of $\rho(\omega)$ at the Fermi level, as was pointed out in [7,8], may be due to a basic feature of the large-d approach, namely, the locality of the self-energy. This is probably connected to the overestimation by a factor of ~ 4 of the enhancement of the calculated mass renormalization compared with that deduced from the measured electronic specific heat coefficient ($\gamma_{\mathrm{exp}} \approx 9.2$ mJ/K^2 mol for $CaVO_3$ [17], this value is about 3 times larger than the LDA prediction). This issue may possibly be resolved by a better treatment of the spatial fluctuations. Nevertheless, we emphasize that the goal of the present paper is not the description of the line shape in its full detail, but rather the understanding of some basic features in the distribution and transfer of spectral weight by the effect of correlations.

We now turn to the comparison of our model results for the optical conductivity [18] with the new experimental data that we report here. The optical reflectivity measurement was carried out for $CaVO_3$, which is the most strongly correlated case. A single crystal sample was grown by the floating zone method and specularly polished. It was annealed in air at ~ 470 K for 24 h in order to make the oxygen concentration become stoichiometric [19]. The reflectivity spectrum was measured at room temperature in energy range from 0.03 to 6.5 eV, using a Fourier transform spectrometer ($0.03 - 0.5$ eV) and a grating monochromator ($0.5 - 6.5$ eV). To obtain the optical conductivity by Kramers-Kronig analysis, we supplemented our data with that of Kasuya *et al.* [20] obtained in a higher energy region. Also, a high frequency asymptotic function of the form ω^{-4} was used, and we extrapolated our data to the lowest frequencies using the Hagen-Rubens formula. The result is displayed in Fig. 2. It basically presents three contributions: a low frequency narrow peak which is the Drude part of the optical conductivity, a second small feature that appears at energies around 1.75 eV, and a third large contribution that peaks at 3.5 eV. The Drude part at low frequencies corresponds to the metallic character of the compound. However, unlike in normal metals, the Drude contribution is only a fraction of the total optical spectral weight. This is a realization of the original arguments of Kohn for the optical response of systems close to a MIT [21].

We can readily, and rather intuitively, interpret the higher frequencies peak structure in terms of excitations between the three features present in the density of states (cf. upper inset of Fig. 1). The large contribution in the conductivity spectrum at $\omega \sim 3.5$ eV corresponds to the direct excitations from the lower to the upper Hubbard bands; therefore, this contribution should peak at an energy of the order of the Hubbard interaction U. Accordingly, the position of the peak very approximately corresponds to twice the energy of the maximum of the

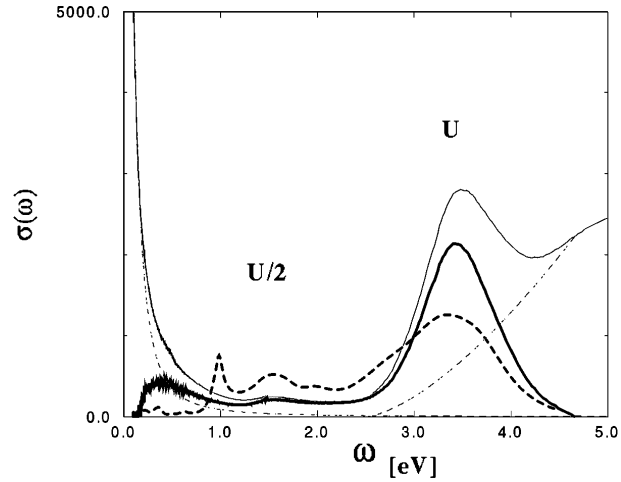

FIG. 2. The experimental optical conductivity $\sigma(\omega)$ in units of $[\Omega\mathrm{cm}]^{-1}$ for $CaVO_3$ at $T = 300$ K (thin line). The midinfrared spectra (bold line) obtained after the subtraction of the background contribution [$\sim (\omega - 2.5\ \mathrm{eV})^{3/2}$] and a Lorentzian fit of Drude part at lower frequencies (thin dashed lines). The model optical conductivity (bold dashed line) for $\frac{U}{D} = 3.2$ and $D = 1$ eV obtained by IPT (arbitrary units).

lower Hubbard band in the photoemission spectrum of Fig. 1. Also, we note that the large spectral weight of this feature corresponds to the fact that most of the single particle spectral weight is concentrated in the incoherent Hubbard bands. On the other hand, we should also expect optical excitations from the LHB to the quasiparticle peak and from this peak to the upper Hubbard band. As the energy for these two types of excitations is approximately $\frac{U}{2}$, they should also contribute to the optical spectrum with a feature at frequencies $\omega \sim \frac{U}{2} \approx 1.75$ eV from the estimation made for this parameter in the photoemission discussion. This is, in fact, observed in the experimental results. We can further understand the small spectral weight of this feature from the fact that the quasiparticle peak in the $\rho(\omega)$ has only a small fraction of the total spectral intensity.

In Fig. 2 we also present the optical spectrum obtained from the LISA method using the model parameters determined before ($x = 1$). We find that all the basic features of our previous qualitative discussion are actually realized in the solution of the model. For a clearer comparison of the model prediction to the experimental data, we have subtracted in the latter the high frequency background due to excitations from the oxygen band to the UHB. From a fit to the lower energy tail of the oxygen band, we estimate this background contribution to start at $\omega \approx 2.5$ eV. Since our model does not contain disorder, the Drude part is a δ function at the origin. Thus, also for the sake of a clear comparison, we have subtracted the Drude part of the experimental spectra by fitting a Lorentzian function at low frequencies. The remaining part of the experimental spectra then corresponds to the midinfrared features at $\frac{U}{2}$ and U that we discussed

above. As the results show, these features are well captured by our model at the precise positions and with qualitatively correct relative weights. As in the case of the photoemission data, the remaining differences in the line shapes may be possibly due to limitations of the IPT or the election of a semicircular ρ^0.

A final quantity that is useful in the interpretation of optical conductivity data is the ratio of the Drude part of the optical response to the total spectral weight. In an uncorrelated system, this ratio is 1. The effect of the correlations that drive the system close to the MIT is to split the contributions to $\sigma(\omega)$ into a δ-function-like part at low frequency that corresponds to the coherent quasiparticle conduction and a regular midinfrared contribution describing the incoherent motion. Within our present mean field theory, this ratio is obtained as $R = Z\frac{\langle K_0\rangle}{\langle K\rangle}$, where Z is the quasiparticle residue and $\langle K_0\rangle$ is the expectation value of the kinetic energy in the free system ($U = 0$) [5,22]. From the experiment we find that $R_{\exp} \approx 0.3$, which is in good agreement with the prediction of the theory $R = 0.25 \pm 0.03$ (the uncertainty comes from the approximate determination of the model parameters U and D and the rapid variation of R close to the MIT). We note that $1/R$ is usually called the optical mass renormalization and that in the $d \to \infty$ limit $\frac{m^*}{m} = 1/Z$. Thus, in our mean field theory these two quantities are exactly related by the renormalization of the kinetic energy by the interaction.

An important observation is that the consistent picture that emerges from our *simultaneous* discussion of photoemission and ac conductivity gives further support to the assumption that a single band model may be used for the study of the $Ca_xSr_{1-x}VO_3$ system. This observation is rather surprising, as the typical magnitude of crystal fields ~ 0.1 eV is unlikely to explain how the 3-fold degeneracy of the t_{2g} bands is effectively lifted. A more plausible explanation may follow from the consideration of a more realistic degenerate model with interorbital exchange and correlation interaction. The solution of such a model poses extra technical challenges and work along this line is currently under way.

Finally, we would like to briefly mention that the temperature dependence of the dc resistivity follows a $\rho \sim AT^2$ behavior which demonstrates that the system is, as our model solution, a Fermi liquid.

The satisfactory agreement between the theory and the experimental data demonstrates that the Hubbard model treated within a mean field theory that becomes exact in the limit of large lattice coordination is indeed a good strating point for the study of electronic systems where the competition of localization and itinerancy plays a crucial role. The LISA solution of the single band model allows us to understand the basic features that are experimentally observed in the spectroscopy of $Ca_xSr_{1-x}VO_3$. We find that the transfer of weight observed in photoemission data and the unusual distribution of spectral weight in the optical response are related to the proximity of the system to a MIT point characterized by the emergence of the small energy scale ϵ_F^* [15]. Thus, we obtain within *a single model with essentially no adjustable parameters*, a consistent interpretation of the unusual features observed in *both* experiments.

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