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Electronic Correlations in Manganites

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The influence of local electronic correlations on the properties of colossal magnetoresistive manganites is investigated. To this end, a ferromagnetic two-band Kondo lattice model is supplemented with the local Coulomb repulsion missing in this model and is analyzed within dynamical mean-field theory. Results for the spectral function, optical conductivity, and the paramagnetic-to-ferromagnetic phase transition show that electronic correlations have drastic effects and may explain some experimental observations.

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The double exchange mechanism [1] is generally considered to be the origin of ferromagnetism in manganites with perovskite structure, like $La_{1-x}Ca_xMnO_3$ or $La_{1-x}Sr_xMnO_3$. Because of the renewed interest in these compounds with respect to their colossal magnetoresistance (CMR) [2], the ferromagnetic Kondo lattice model [(KLM), also known as the *s-d* model] has recently been investigated intensively [3–5] as the microscopic basis of double exchange. Because of the crystal-field splitting of the five Mn *d*-orbitals into three degenerate t_{2g}-orbitals and two degenerate e_g-orbitals at a higher energy level, three t_{2g} electrons can be approximately modeled as a spin 3/2, with the remaining $n = 1 - x$ electrons occupying the e_g-orbitals. The latter are delocalized via an effective double exchange transfer [1] t which is mediated by the overlap between Mn e_g- and O p-orbitals. This transfer, together with the local Hund's rule exchange $J > 0$ between t_{2g} and e_g spins, constitutes the ferromagnetic KLM

$$\hat{H}_{\mathrm{KLM}} = -t \sum_{\nu=1}^{2} \sum_{\langle ij \rangle} \hat{c}_{i\nu\sigma}^{\dagger} \hat{c}_{j\nu\sigma} - 2J \sum_{\nu=1}^{2} \sum_{i} \hat{\mathbf{s}}_{i\nu} \hat{\mathbf{S}}_i \,. \quad (1)$$

Here $\hat{c}_{i\nu\sigma}^{\dagger}$ and $\hat{c}_{i\nu\sigma}$ are creation and annihilation operators for electrons on site i within e_g-orbital ν with spin σ; $\hat{\mathbf{s}}_{i\nu} = \frac{1}{2} \sum_{\sigma\sigma'} \hat{c}_{i\nu\sigma}^{\dagger} \boldsymbol{\tau}_{\sigma\sigma'} \hat{c}_{i\nu\sigma'}$ denotes the e_g spin ($\boldsymbol{\tau}$: Pauli matrices), $\hat{\mathbf{S}}_i$ the t_{2g} spin, and $\langle ij \rangle$ is the sum over all sites and their neighbors. At doping x, $\sum_{\nu\sigma} \langle \hat{c}_{i\nu\sigma}^{\dagger} \hat{c}_{i\nu\sigma} \rangle = 1 - x$. To keep the model approach simple, the transfer t between electrons on neighboring Mn sites is assumed to be diagonal in the orbital index and independent of the lattice direction.

For $J \gg t$, the e_g electrons are oriented parallel to the t_{2g} spins. With this constraint, a ferromagnetic alignment of the t_{2g} spins allows for a maximal kinetic energy gain of the e_g electrons. This double exchange mechanism is generally considered to be responsible for ferromagnetism in manganites. However, it was pointed out by Millis *et al.* [6] that double exchange alone cannot describe the resistivity of manganites. In particular, the importance of electron-lattice coupling was stressed [7,8] and the effect of lattice polarons and bipolarons was studied [6,7,9]. The effect of Anderson localization [10], tunneling magnetoresistance between phase separated domains [5], and orbital polarons [11] was also investigated. In spite of this, the unusual properties of the paramagnetic "insulating" phase of manganites which shows a (quasi-) gap in the photoemission spectrum [12] and in the optical conductivity [13] for arbitrary doping x are not yet sufficiently understood.

In this Letter we emphasize the importance of electronic correlations due to the local Coulomb repulsion for understanding the properties of manganites. These correlations are neglected in the KLM (1). This neglect is *a priori* unjustified in regard to the fact that the electronic repulsion is known to be the largest energy in the problem, and it originated only in the technical difficulties of the ensuing many-body problem. Presently, the best manageable approach for this type of problem is the dynamical mean-field theory (DMFT) [14,15]. We use this approach here and show that (i) electronic correlations have a pronounced effect on the paramagnetic phase, yielding an upper Hubbard band in the spectral function and a shift of spectral weight as is observed experimentally, and that (ii) the microscopic origin of ferromagnetism *changes* from double exchange at doping $0.5 \lesssim x \leq 1$ to superexchange at $x \to 0$.

A correlated electron model taking into account the Coulomb repulsion between e_g electrons has the form

$$\hat{H} = \hat{H}_{\mathrm{KLM}} + U \sum_{\nu=1}^{2} \sum_{i} \hat{n}_{i\nu\uparrow} \hat{n}_{i\nu\downarrow} + \sum_{i\sigma\tilde{\sigma}} (V_0 - \delta_{\sigma\tilde{\sigma}} F_0) \hat{n}_{i1\sigma} \hat{n}_{i2\tilde{\sigma}} \,. \quad (2)$$

Here, $\hat{H}_{\mathrm{KLM}}$ is the KLM (1) for an Ising-type t_{2g} spin of size $|S_i^z| = 1$ [16], $\hat{n}_{i\nu\sigma} = \hat{c}_{i\nu\sigma}^{\dagger} \hat{c}_{i\nu\sigma}$, U and V_0 are the on-site Coulomb repulsions within the same and different e_g orbitals, respectively, and F_0 is the Ising component of the Hund's rule exchange coupling between e_g spins. From band structure calculations [17] and photoemission plus x-ray absorption experiments [18,19] these parameters are estimated as $U, V_0 \approx 8$ eV and $F_0, J \approx 1$ eV. The band structure results for the e_g bandwidth $W = 1$–2 eV [17] are somewhat smaller than that measured ($W = 3$–4 eV [12]). Up to now, the Coulomb repulsion was taken into account only in two limits. First, at $x = 0$ the correlated electron model maps onto an effective

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Kugel'-Khomskiĭ-type model at strong Coulomb repulsion [20]. Here, magnetism is obtained in second-order perturbation theory in t from superexchange. Second, the fully spin-polarized phase, where the correlated electron model reduces to a one-band Hubbard or t-J model in the orbital degrees of freedom, was studied [21]. Even the analysis of the one-dimensional problem is very demanding.

To solve Eq. (2), we employ DMFT where the lattice model (2) maps onto a self-consistent single-site problem for the Green function

$$G_{\nu\sigma n} = \frac{-1}{\mathcal{Z}} \sum_{S^z=\pm 1} \int D\Psi\, D\Psi^*\, \Psi_{\nu\sigma n}\Psi^*_{\nu\sigma n} \times e^{\mathcal{A}[\Psi^*,\Psi,S^z,\mathcal{G}^{-1}]} \tag{3}$$

with $\mathcal{G}^{-1} = G^{-1} + \Sigma$ (Σ: self-energy), partition function $\mathcal{Z} = \sum_{S^z=\pm 1} \int D[\Psi]\, D[\Psi^*] \exp \mathcal{A}[\Psi^*, \Psi, S^z, \mathcal{G}^{-1}]$, Grassmann variables $\Psi_{\nu\sigma n}$ and $\Psi^*_{\nu\sigma n}$ at Matsubara frequencies $\omega_n = (2n + 1)\pi/\beta$, and

$$\mathcal{A}[\Psi^*, \Psi, S^z, \mathcal{G}^{-1}] = \sum_{\nu\sigma n} \psi^*_{\nu\sigma n}[\mathcal{G}^{-1}_{\nu\sigma n} + \sigma J S^z]\psi_{\nu\sigma n} - U \sum_{\nu} \int_0^\beta d\tau\, \psi^*_{\nu\uparrow}(\tau)\psi_{\nu\uparrow}(\tau)\psi^*_{\nu\downarrow}(\tau)\psi_{\nu\downarrow}(\tau) - \sum_{\nu<\nu';\sigma\sigma'} (V_0 - \delta_{\sigma\sigma'}F_0) \int_0^\beta d\tau\, \psi^*_{\nu\sigma}(\tau)\psi_{\nu\sigma}(\tau)\psi^*_{\nu'\sigma'}(\tau)\psi_{\nu'\sigma'}(\tau)\,.$$

The single-site problem (3) is solved numerically by quantum Monte Carlo (QMC) simulations using a two-band version of the Hirsch-Fye algorithm [22]. Employing the symmetry $S^z_i \to -S^z_i, G_\sigma \to G_{-\sigma}$ in the paramagnetic phase, only one of two local Ising configurations of (3) needs to be calculated. The mean value of spin-up and spin-down Green functions for this Ising configuration yields the paramagnetic Green function. Self-consistency is obtained by iterating (3) with the $\mathbf{k}$-integrated Dyson equation

$$G_{\nu\sigma n} = \int_{-\infty}^{\infty} d\varepsilon\, \frac{N^0(\varepsilon)}{i\omega_n + \mu - \Sigma_{\nu\sigma n} - \varepsilon}\,, \tag{4}$$

where $N^0(\varepsilon) = \frac{1}{\pi W^2/8}\sqrt{(W/2)^2 - \varepsilon^2}$ is the noninteracting density of states with bandwidth W.

The QMC algorithm yields the Green function at imaginary Matsubara frequencies. To obtain the Green function $G_{\nu\sigma}(\omega)$ as a function of real frequencies an analytic continuation employing the maximum entropy method [23] is performed. The resulting spectral function $A_{\nu\sigma}(\omega) = -\mathrm{Im}G_{\nu\sigma}(\omega)/\pi$ for the paramagnetic phase is shown in Fig. 1 at $n = 0.7$, $W = 2$, $U = 8$,$V_0 = 6$, and $F_0 = 1$. In units of eV these are realistic parameters for manganites if W is identified with its band structure value. For comparison the dotted line shows the results for the ferromagnetic KLM ($U = V_0 = F_0 = 0$) which was solved following Furukawa [5]. Without local Coulomb repulsion, the spectral function consists of two bands corresponding to configurations with e_g spin parallel and antiparallel to the t_{2g} spin. Some of these configurations contain doubly occupied sites. Thus a Hubbard band at the energy U,V_0 is expected to develop once this repulsion is taken into account. Indeed, the drastic changes shown in Fig. 1 illustrate this effect, which goes along with a shift of spectral weight from the lower band at the Fermi energy ($\omega = 0$) to the upper band, for $x > 0$ [24]. Such a transfer of spectral weight is observed experimentally in the doped system [19]. In view of the present results this effect may be attributed to electronic correlations. Another effect of electronic correlations is the broadening of the bandwidth due to the imaginary part of the self-energy. This may account for the discrepancy between the bandwidth obtained by band structure calculations [17] and the photoemission experiment [12]. While electronic correlations can explain some aspects of the manganite spectrum, the spectral weight at the Fermi level itself none the less remains large. We cannot exclude that the exact treatment of the three-dimensional model may explain the unusual nature of the paramagnetic phase. But, at least within DMFT, electronic correlations alone can also not fully elucidate the unusual properties of the insulating paramagnetic phase of CMR manganites.

Next we calculate the optical conductivity. Within DMFT this quantity is obtained from the particle-hole diagram only, since, in this limit, vertex corrections to the optical conductivity vanish [25]. Following [15] we employ the formula

$$\mathrm{Re}\sigma(\omega) = -\frac{1}{\pi} \int d\varepsilon\, N^0(\varepsilon) \int_{-\infty}^{\infty} d\omega'\, \mathrm{Im}G_{\boldsymbol{\varepsilon}}(\omega') \times \mathrm{Im}G_{\boldsymbol{\varepsilon}}(\omega' + \omega)\, \frac{f(\omega) - f(\omega' + \omega)}{\omega}\,, \tag{5}$$

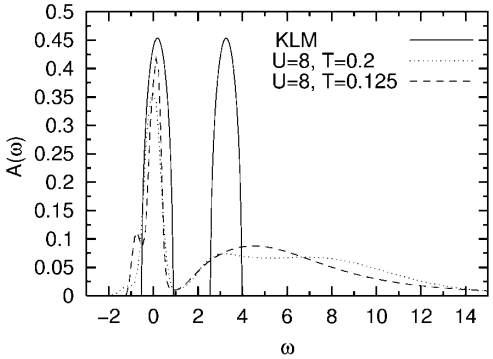

FIG. 1. Spectral function $A(\omega)$ ($\omega = 0$ corresponds to the Fermi energy) for the manganite model (2) at doping $x = 0.3$, $W = 2$, $U = 8$, $F_0 = 1$, $V_0 = U - 2F_0$, and $J = 3/2F_0$. Electronic correlations yield a satellite band at about V_0 and a shift of spectral weight from the lower band at the Fermi energy to higher energies.

as derived for the hypercubic lattice by Pruschke *et al.* [25]. Here $\mathrm{Im}G_{\boldsymbol{\varepsilon}}$ is the imaginary part of

$$G_{\boldsymbol{\varepsilon}}(\omega) = \frac{1}{\omega + i\delta + \mu - \Sigma(\omega) - \varepsilon}. \qquad (6)$$

The result is shown in Fig. 2. Already for $U = V_0 = F_0 = 0$ (ferromagnetic KLM) the optical conductivity deviates considerably from the results for the noninteracting system ($J = 0$). This is due to the scattering of the e_g electrons at the disordered t_{2g} spins which leads to a non-Fermi liquid paramagnetic phase with a finite imaginary part of the self-energy at the Fermi energy. Electronic correlations induced by the local Coulomb repulsion further reduce the optical conductivity at small frequencies. A second peak (absent for $J = 0$), which results from contributions to the particle-hole diagram with particles in the upper band and holes in the lower band of the spectrum, is smeared out by the electronic correlations.

Finally, we investigate the instability of the paramagnetic phase against long-range ferromagnetic order. To this end, we calculate the magnetic susceptibility $\chi(T)$ which diverges at the Curie temperature T_c as $\chi(T) = a(T - T_c)^{-1}$ within DMFT. Figure 3 shows the results as a function of doping x together with two analytically tractable limits of DMFT: (i) double exchange (dashed line) as described by the ferromagnetic KLM and (ii) superexchange (cross) at $x = 0$ and strong coupling. The KLM [case (i)] neglects electronic correlations and, at $J \gg t$, leads to double exchange with an energy gain proportional to the kinetic energy gain of the e_g electrons in a ferromagnetic environment, i.e., $T_c \propto t$. At $x = 1$ the e_g bands are empty and no kinetic energy is gained, i.e., $T_c = 0$. On the other hand, at $x = 0$, the two spin-polarized e_g bands are half filled, such that the kinetic energy gain, and hence T_c, is maximal. In case (ii), DMFT corresponds to Weiss mean-field theory for the effective Kugel'-Khomskiĭ-type Hamiltonian which, at $x = 0$, predicts an instability against orbital ordering and an additional instability against ferromagnetic order at $T_c = Zt^2/(V_0 - F_0) - Zt^2/(V_0 + 2J)$ (Z: number of nearest neighbors). Since $t \ll U, V_0$ the critical temperature of the superexchange mechanism ($T_c \propto t^2/V_0$) is an order of magnitude *smaller* than that of double exchange ($T_c \propto t$).

Solving the correlated electron model (2) for arbitrary x numerically within DMFT, a *crossover* from double exchange to superexchange is clearly observed. At $x \gtrsim 0.5$, the critical temperature is relatively well described by the ferromagnetic KLM, i.e., by double exchange. Here, double occupations are rare since there are only a few e_g electrons. With decreasing x (increasing the number of e_g electrons) the local Coulomb repulsion strongly reduces double occupancies and thus becomes more and more important. The kinetic energy gain, and thereby double exchange, is reduced and superexchange becomes effective instead. This crossover from double exchange to superexchange yields a *maximum* in T_c in qualitative agreement with experiment. Note that without the coupling to the t_{2g} spin, i.e., in a two-band Hubbard model, no ferromagnetism was observed for $0 \leq n < 1$ at values of F_0 typical for manganites [26].

In conclusion, our results show that electronic correlations are certainly important for understanding CMR manganites and cannot be neglected. In the paramagnetic phase, electronic correlations lead to the formation of an upper Hubbard band and to a shift of spectral weight into this band if the system is doped. This shift of spectral weight from a lower to an upper band is a genuine correlation effect and may explain a similar experimental observation [19]. Another aspect of electronic correlations is the broadening of the spectrum due to the imaginary part of

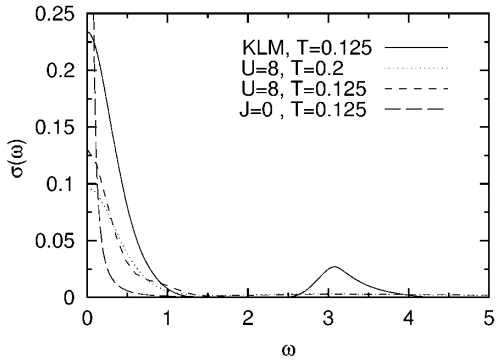

FIG. 2. Optical conductivity $\sigma(\omega)$ at $x = 0.3$, $W = 2$, $U = 8$, $F_0 = 1$, $V_0 = 6$, and $J = 3/2$. Dotted line: $T = 0.2$; short-dashed line: $T = 0.125$; solid line: KLM ($U = F_0 = V_0 = 0$); long-dashed line: noninteracting system ($J = U = F_0 = V_0 = 0$; line broadening $\delta = 0.01$). The optical conductivity of the interacting system is seen to differ considerably from that of a Fermi liquid.

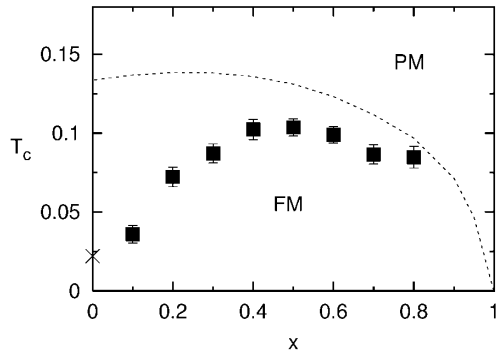

FIG. 3. Curie temperature T_c for the phase transition from the paramagnetic (PM) to the ferromagnetic (FM) phase as a function of doping x. Dashed line: KLM with $W = 2$ and $J = 3/2$; squares: correlated electron model (2) which also takes into account the Coulomb interaction between e_g electrons ($U = 8$, $V_0 = 6$, and $F_0 = 1$); cross: Weiss mean-field theory for (2). The correlated electron model is seen to describe a crossover from double exchange at $0.5 \lesssim x \leq 1$ to superexchange at $x \to 0$.

the self-energy. This might be the reason why band structure calculations yield only about half of the spectral width compared to the photoemission experiment. The main result for the paramagnetic-to-ferromagnetic phase transition is that double exchange, as described by the ferromagnetic KLM, can explain ferromagnetism in CMR manganites only for doping $x \gtrsim 0.5$. At lower values of x, the suppression of double occupations by the local Coulomb repulsion becomes more and more important and leads to a crossover from double exchange to superexchange. This results in a maximum of the Curie temperature in qualitative agreement with experiment.

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[1] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[2] The renewed interest in these compounds began with R. M. Kusters *et al.,* Physica (Amsterdam) **155B**, 362 (1989); R. von Helmolt *et al.,* Phys. Rev. Lett. **71**, 2331 (1992); K. Chahara *et al.,* Appl. Phys. Lett. **63**, 1990 (1993); S. Jin *et al.,* Science **264**, 413 (1994); P. Schiffer *et al.,* Phys. Rev. Lett. **75**, 3336 (1995); for a recent phase diagram of $La_{1-x}Sr_xMnO_3$, see M. Paraskevopoulos *et al.,* J. Magn. Magn. Mater. **211**, 118 (2000); for reviews, see A. P. Ramirez, J. Phys. Condens. Matter **9**, 8171 (1997); E. L. Nagaev, Phys. Usp. **39**, 781 (1996).

[3] S. Yunoki, A. Moreo, and E. Dagotto, Phys. Rev. Lett. **81**, 5612 (1998); cond-mat/9901057; in *Proceedings of the Workshop Physics in Manganites,* edited by T. A Kaplan and S. D. Mahanti (Michigan State University, East Lansing, 1998); E. Müller-Hartmann and E. Dagotto, Phys. Rev. B **54**, 6819 (1996); M. J. Calderón and L. Brey, Phys. Rev. B **58**, 3286 (1998); D. P. Arovas and F. Guinea, Phys. Rev. B **58**, 9150 (1998); J. van den Brink and D. I. Khomskiĭ, Phys. Rev. Lett. **82**, 1016 (1999).

[4] S. Yunoki *et al.,* Phys. Rev. Lett. **80**, 845 (1998).

[5] N. Furukawa, J. Phys. Soc. Jpn. **63**, 3214 (1994); in *Proceedings of the Workshop Physics in Manganites* (Ref. [3]).

[6] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

[7] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[8] G.-M. Zhao *et al.,* Nature (London) **381**, 676 (1996).

[9] H. Röder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996); J. D. Lee and B. I. Min, Phys. Rev. B **55**, 12 454 (1997); A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. Lett. **82**, 141 (1999).

[10] C. M. Varma, Phys. Rev. B **54**, 7328 (1996).

[11] R. Kilian and G. Khaliullin, Phys. Rev. B **60**, 13 458 (1999).

[12] J.-H. Park *et al.,* Phys. Rev. Lett. **76**, 4215 (1996); T. Saitoh *et al.,* Phys. Rev. B **56**, 8836 (1997).

[13] K. H. Kim, J. H. Jung, and T. W. Noh, Phys. Rev. Lett. **81**, 4983 (1998).

[14] W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989); E. Müller-Hartmann, Z. Phys. B **74**, 507 (1989); A. Georges and G. Kotliar, Phys. Rev. B **45**, 6479 (1992); M. Jarrell, Phys. Rev. Lett. **69**, 168 (1992); D. Vollhardt, in *Correlated Electron Systems,* edited by V. J. Emery (World Scientific, Singapore, 1993), p. 57; T. Pruschke, M. Jarrell, and J. K. Freericks, Adv. Phys. **44**, 187 (1995).

[15] A. Georges *et al.,* Rev. Mod. Phys. **68**, 13 (1996).

[16] The replacement of a spin $3/2$ by a classical spin (which is equivalent to an Ising spin in the paramagnetic phase within DMFT [5]) is the standard approach to manganite models. Though this approximation neglects the dynamics of the spins and is justified only for rather large spins, recent results for the KLM found a good agreement between a spin $3/2$ and a classical spin [4]. Using $|S_i^z| = 1$ instead of $|S_i^z| = 3/2$ just renormalizes J by $3/2$.

[17] See, e.g., S. Satpathy, Z. S. Popović, and F. R. Vukajlović, Phys. Rev. Lett. **76**, 960 (1996); A. Singh and W. E. Pickett, Phys. Rev. B **57**, 88 (1998).

[18] A. E. Bocqeut *et al.,* Phys. Rev. B **46**, 3771 (1992).

[19] T. Saitoh *et al.,* Phys. Rev. B **51**, 13 942 (1995).

[20] S. Ishihara, J. Inoue, and S. Maekawa, Phys. Rev. B **55**, 8280 (1997); R. Shiina, T. Nishitani, and H. Shiba, J. Phys. Soc. Jpn. **66**, 3159 (1997); L. F. Feiner and A. M. Oleś, Phys. Rev. B **59**, 3295 (1999).

[21] M. Imada, J. Phys. Soc. Jpn. **67**, 45 (1998); Y. Motome and M. Imada, J. Phys. Soc. Jpn. **68**, 16 (1999); M. J. Rozenberg, Eur. Phys. J. B **2**, 457 (1998); V. Ferrari and M. J. Rozenberg, cond-mat/9906131; R. Kilian and G. Khaliullin, Phys. Rev. B **58**, 11 841 (1998).

[22] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986).

[23] For a review on the maximum entropy method, see M. Jarrell and J. E. Gubernatis, Phys. Rep. **269**, 133 (1996).

[24] Note that due to uncertainties of the maximum entropy method at large $|\omega|$ a possible inner structure of the upper band is difficult to resolve.

[25] T. Pruschke, D. L. Cox, and M. Jarrell, Phys. Rev. B **47**, 3553 (1993).

[26] K. Held and D. Vollhardt, Euro. Phys. J. B **5**, 473 (1998).