Photoemission Quasiparticle Spectra of Sr_2RuO_4

A. Liebsch* and A. Lichtenstein†

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

(Received 21 September 1999)

Multiband quasiparticle calculations based on perturbation theory and dynamical mean-field methods show that the creation of a photoemission hole state in Sr_2RuO_4 is associated with a highly anisotropic self-energy. Since the narrow Ru-derived $d_{xz,yz}$ bands are more strongly distorted by Coulomb correlations than the wide d_{xy} band, charge is partially transferred from $d_{xz,yz}$ to d_{xy}, thereby shifting the d_{xy} Van Hove singularity close to the Fermi level.

PACS numbers: 74.70.Ad, 73.20.Dx, 74.80.Dm, 79.60.Bm

Angle-resolved photoemission spectroscopy is one of the key techniques providing detailed information on the Fermi surface topology of high temperature superconductors. In the layered copper oxide compounds (cuprates) high-resolution photoemission spectra can be obtained below and above the superconducting transition temperature and for different hole doping regimes. Although de Haas–van Alphen (dHvA) experiments in principle yield more reliable bulk Fermi surface data, they are less useful for the investigation of cuprates since they require extremely pure samples. Thus, it has so far not been possible for any of the high T_c cuprates to obtain consistent Fermi surface data from both photoemission and dHvA measurements.

The detection of superconductivity in Sr_2RuO_4 [1] is of great importance since this system is the only layered perovskite compound known so far that is superconducting in the absence of copper and without requiring doping. Thus, a critical comparison of photoemission Fermi surface data with those derived from dHvA measurements is feasable. Surprisingly, independent studies of the dHvA effect [2] and angle-resolved photoemission [3–5] yield highly contradictory Fermi surface topologies. This discrepancy raises serious questions concerning the interpretation of photoemission data also in cuprate superconductors.

Because of the layered structure of Sr_2RuO_4, the electronic bands close to the Fermi level may be qualitatively understood in terms of a simple tight-binding picture. These bands are derived mainly from Ru t_{2g} states. The wide xy band exhibits two-dimensional character, while the narrow xz and yz bands are nearly one dimensional. All three bands are roughly $2/3$ occupied, giving about 4 Ru d electrons per formula unit. Density functional calculations based on the local density approximation (LDA) [6,7] place the $(\pi, 0), (0, \pi)$ saddle point Van Hove singularity of the xy band about 60 meV *above* the Fermi energy. Taking into account gradient corrections slightly lowers this singularity to about 50 meV above E_F [7]. Figure 1 provides a qualitative picture of the t_{2g} bands and of the Fermi surface exhibiting one hole sheet (α) and two electron sheets (β, γ). Whereas the dHvA data [2] are consistent with these results, photoemission spectra reveal a fundamentally different topology [3–5]: the xy Van Hove singularity near M appears *below* the Fermi level, converting the γ sheet from electronlike to holelike. Nevertheless, both experiments are reported to be in accord with Luttinger's theorem.

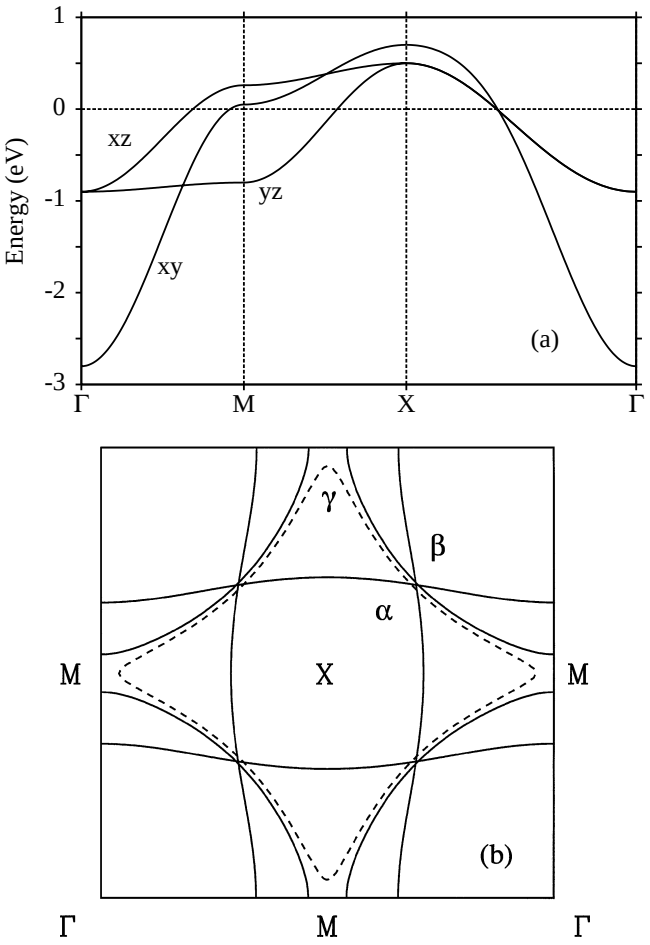

FIG. 1. (a) Dispersion of t_{2g} bands of Sr_2RuO_4 in simplified two-dimensional Brillouin zone ($E_F = 0$). (b) Solid lines: Fermi surface consistent with LDA band structure and dHvA measurements, with hole sheet α and electron sheets β, γ (after accounting for hybridization). Dashed line: approximate xy Fermi surface derived from photoemission, indicating that γ is holelike.

Various effects have been proposed to explain this discrepancy between dHvA and photoemission data. (a) Since photoemission is surface sensitive, a surface-induced reconstruction associated with the breaking of bonds could lead to a modification of Ru-O hopping and a shift of t_{2g} bands. Estimates based on bulk calculations indicate that this mechanism could push the xy Van Hove singularity below E_F [7]. Actual surface electronic structure calculations for Sr_2RuO_4 [8], however, show that this singularity remains above E_F even in the presence of surface relaxation. (b) Slightly different doping levels, temperatures, and magnetic fields used in both experiments could result in different Fermi surfaces, but these effects are believed to be too small to explain the main discrepancy [9]. (c) That the interpretation of the dHvA data is incorrect seems unlikely in view of the large body of experience available for this method. (d) The interpretation of the photoemission spectra, on the other hand, is nontrivial because of the quasiparticle character of the hole state created in the experiment. This aspect of the data has been ignored so far and is the focus of the present work.

According to the reduced dimensionality of Sr_2RuO_4, creation of a photohole should be associated with highly anisotropic screening processes which reflect the nature of the different electronic states involved. As shown in Fig. 1, the relevant bands near E_F comprise a roughly 3.5 eV wide band formed by in-plane hopping between Ru d_{xy} and O $2p$ orbitals, and 1.4 eV narrow d_{xz}, d_{yz} bands. Assuming an on-site Ru dd Coulomb interaction $U \approx 1.5$ eV, we have the intriguing situation: $W_{xz,yz} < U < W_{xy}$, where W_i is the width of the ith t_{2g} band. A value $U \approx 1.5$ eV was in fact deduced from the observation of a valence band satellite in resonant photoemission from Sr_2RuO_4 [10]. According to this picture, intra-atomic correlations have a much larger effect on the xz, yz bands than on the xy band, giving rise to a strongly anisotropic self-energy. Because of the $\sim 2/3$ filling of the xz, yz bands, their narrowing, combined with Luttinger's theorem, leads to a charge flow from the xz, yz bands to the xy band. As we discuss below, for reasonable values of U this charge transfer is large enough to push the xy Van Hove singularity close to or even below the Fermi level.

Since we are concerned with the qualitative influence of multiband correlations on quasiparticle spectra, we consider for simplicity two-dimensional next-nearest-neighbor tight-binding bands of the form $\varepsilon(k) = -\varepsilon_0 - 2t_x \cos ak_x - 2t_y \cos ak_y + 4t' \cos ak_x \times \cos ak_y$, where $(\varepsilon_0, t_x, t_y, t') = (0.50, 0.44, 0.44, -0.14)$, $(0.24, 0.31, 0.045, 0.01)$, $(0.24, 0.045, 0.31, 0.01)$ eV for xy, xz, yz, respectively (see Fig. 1). These parameters ensure that the xy band has edges at -2.8 and 0.7 eV, with a Van Hove singularity at 0.05 eV, and the xz, yz bands have edges at -0.9 and 0.5 eV, with Van Hove singularities at -0.80 and 0.26 eV, in agreement with the LDA band structure [7].

Next we specify the on-site Coulomb and exchange integrals which we use in the self-energy calculations discussed below. In the present case involving only t_{2g} states, there are three independent elements ($i \neq j$) [11]: $U = \langle ii||ii\rangle$, $U' = \langle ij||ij\rangle$, and $J = \langle ij||ji\rangle = \langle ii||jj\rangle = (U - U')/2$, where $i = 1, \ldots, 3$ refers to xy, xz, yz. Denoting by n_i the band occupations, the Hartree-Fock energies are $\Sigma_1^{\mathrm{HF}} = (n_1 + 4n_2)U - 10n_2J$ and $\Sigma_{2,3}^{\mathrm{HF}} = (2n_1 + 3n_2)U - 5(n_1 + n_2)J$. As the band occupations n_i are rather similar, it is convenient to define the average occupation $\bar{n}$, so that $n_1 = \bar{n} - 2\delta$, $n_{2,3} = \bar{n} + \delta$, and $\Sigma_1^{\mathrm{HF}} = 5\bar{n}(U - 2J) + 2\delta(U - 5J)$, $\Sigma_{2,3}^{\mathrm{HF}} = 5\bar{n}(U - 2J) - \delta(U - 5J)$.

It is instructive to consider the second-order contribution to the local self-energy since the key point, namely, the large difference between the quasiparticle shifts of the xy and xz, yz bands, can already be illustrated in this approximation. Because the t_{2g} bands do not hybridize, the self-energy has no off-diagonal elements. The imaginary parts of the diagonal second-order Coulomb and exchange terms are given by

$$\mathrm{Im}\Sigma_i(\omega) = \pi \sum_{jkl} R_{jkl}(\omega) \langle ij||kl\rangle [2\langle kl||ij\rangle - \langle kl||ji\rangle], \tag{1}$$

where

$$R_{jkl}(\omega) = \left(\int_0^\infty \int_{-\infty}^0 \int_{-\infty}^0 + \int_{-\infty}^0 \int_0^\infty \int_0^\infty \right) d\omega_1\, d\omega_2\, d\omega_3\, \rho_j(\omega_1)\rho_k(\omega_2)\rho_l(\omega_3)\delta(\omega + \omega_1 - \omega_2 - \omega_3). \tag{2}$$

Here, $\rho_j(\omega)$ denotes the single-particle density of t_{2g} states. Exploiting the symmetry properties of the Coulomb matrix elements, Eq. (1) reduces to

$$\mathrm{Im}\Sigma_1(\omega) = U^2 R_{111}(\omega) + 2J^2 R_{122}(\omega) + 4(U'^2 + J^2 - U'J) R_{212}(\omega), \tag{3}$$

$$\mathrm{Im}\Sigma_{2,3}(\omega) = (U^2 + 2U'^2 + 3J^2 - 2U'J) R_{222}(\omega) + J^2 R_{211}(\omega) + 2(U'^2 + J^2 - U'J) R_{112}(\omega). \tag{4}$$

The above expressions demonstrate that even for $J = 0$ the self-energy of a given band depends on scattering processes involving all three t_{2g} bands. Nevertheless, Σ_{xy} is dominated by interactions within the wide xy band or between xy and xz, yz. On the other hand, $\Sigma_{xz,yz}$ primarily depends on interactions within the narrow xz, yz bands or between xz, yz and xy. These differences are a consequence of the layered structure of Sr_2RuO_4 and give rise to anisotropic relaxation shifts.

For a more accurate description of charge transfer among quasiparticle bands, we include self-consistency in the spirit of dynamical mean-field theory [12]. In this scheme, Σ_i is a functional of the effective bath

Green's function $\mathcal{G}_i^{-1} = G_i^{-1} + \Sigma_i$, where the local G_i is given by

$$G_i(\omega) = \int_{-\infty}^{\infty} d\omega' \, \frac{\rho_i(\omega')}{\omega + \mu - \Sigma_i(\omega) - \omega'} . \quad (5)$$

A typical frequency variation of Σ_i is shown in Fig. 2. Near E_F, the imaginary parts vary quadratically with frequency and the real parts satisfy $\Sigma_{xz,yz} \gg \Sigma_{xy}$; i.e., the energy shift of the narrow xz, yz bands is much larger than for the wide xy band. Moreover, the difference $\Sigma_{xz,yz} - \Sigma_{xy}$ at E_F is much larger than the difference between the Hartree-Fock energies $\Sigma_{xz,yz}^{\mathrm{HF}} - \Sigma_{xy}^{\mathrm{HF}}$.

Qualitatively similar results are derived from more refined treatments of on-site Coulomb correlations using multiband self-consistent quantum Monte Carlo (QMC) methods [12,13]. The temperature of the simulation was 15 meV with 128 imaginary time slices and ~300 000 Monte Carlo sweeps. Figure 3 shows the quasiparticle density of states $N_i(\omega) = -\frac{1}{\pi} \mathrm{Im} G_i(\omega)$, obtained via maximum entropy reconstruction [14], together with the bare density of states $\rho_i(\omega)$. The Van Hove singularities near the edges of the xz, yz bands are shifted towards E_F, causing a sizable band narrowing. Because of the $\sim 2/3$ filling of these bands, this effect is not symmetric, giving a stronger relaxation shift of the occupied bands than for the unoccupied bands. There is also some band narrowing of the xy bands, but since $U < W_{xy}$ this effect is much smaller than for the xz, yz bands.

A crucial point is now that in order to satisfy the Luttinger theorem the more pronounced band narrowing of the xz, yz bands requires a transfer of spectral weight to the xy bands. Thus, the xy Van Hove singularity is pushed towards the Fermi level. In the example shown in Fig. 3, it lies about 10 meV above E_F, compared to 50 meV in the single-particle spectrum. We emphasize that this result is a genuine multiband effect where the filling of a relatively wide quasiparticle band is modified by correlations within other narrow bands of a different symmetry. Since the values of U and J are not well known, and considering the approximate nature of our single-particle bands and self-energy calculations, it is not possible at the present to predict the exact position of the xy singularity. It is conceivable, therefore, that this saddle point might lie even closer to or below E_F.

As indicated in Fig. 1, the topology of the Fermi surface of Sr_2RuO_4 depends critically on the position of the xy Van Hove singularity with respect to E_F. It is evident therefore that the charge transfer from xz, yz to xy due to the creation of the photohole must be taken into account when using angle-resolved photoemission to determine the shape of the Fermi surface. To compare our results with photoemission spectra, we show in Fig. 4(a) the dispersion of the t_{2g} quasiparticle bands along ΓM and MX derived from the spectral function $A_i(\mathbf{k}, \omega) = -\frac{1}{\pi} \mathrm{Im}[\omega + \mu - \varepsilon_i(\mathbf{k}) - \Sigma_i(\omega)]^{-1}$. The xy Van Hove singularity at M lies 10 meV above E_F, so that considerable spectral weight appears below E_F in the immediate vicinity of M. To account for the finite energy resolution, and following the experimental procedure for determining the spectral weight near E_F [5], we show in Fig. 4(b) the Fermi surface obtained from the partially integrated spectral function $\bar{A}_i(\mathbf{k}) = \int_{-\Delta}^{\Delta} d\omega \, A_i(\mathbf{k}, \omega + i\Delta)$ with $\Delta = 25$ meV. Considering in addition the finite aperture of the detector (typically $\pm 1°$, corresponding to $\pm 5\%$ of $k_\parallel$ near M for 25 eV photon energy), it is unavoidable to pick up spectral weight from occupied regions near M, even when the detector is nominally set at M. Thus, the near degeneracy of the xy singularity with E_F makes it extremely difficult using angle-resolved photoemission to determine the k point at which the xy band crosses the Fermi energy. Photoemission data taken with better energy and angle resolution might provide a more conclusive answer.

Figures 3 and 4 also show that due to the narrowing of the xz, yz bands, the weakly dispersive band is shifted from -0.8 to about -0.4 eV, in agreement with photoemission data [3–5]. For $k_\parallel$ between M and X, this band is observed to cross E_F at about $(\pi, 0.6\pi)$, in good accord with our calculations. In addition, the calculations indicate the existence of a satellite below the xz, yz bands which might be

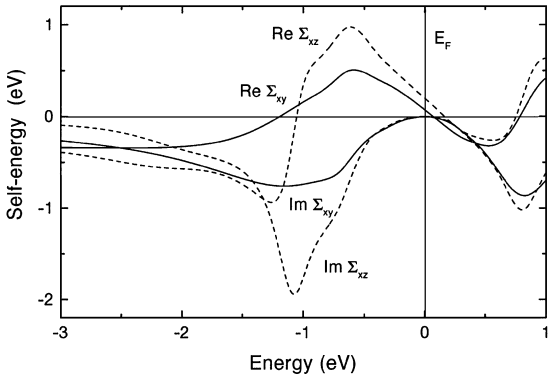

FIG. 2. Real and imaginary parts of self-consistent second-order self-energy for $U = 1.2$ eV, $J = 0.2$ eV. Solid curves: xy; dashed curves: xz.

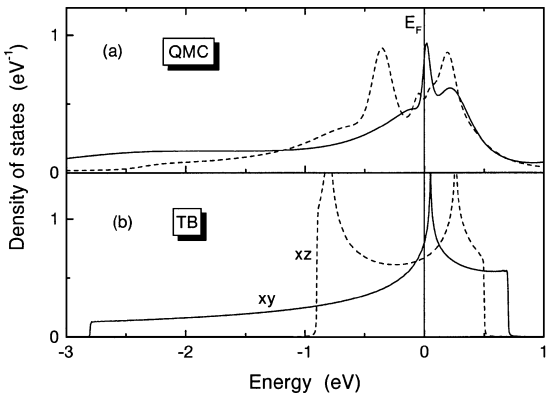

FIG. 3. (a) Quasiparticle density of states $N_i(\omega)$ derived from self-consistent QMC scheme for $U = 1.2$ eV, $J = 0.2$ eV. (b) Single-particle density of states $\rho_i(\omega)$ derived from tight-binding bands. Solid curves: xy; dashed curves: xz.

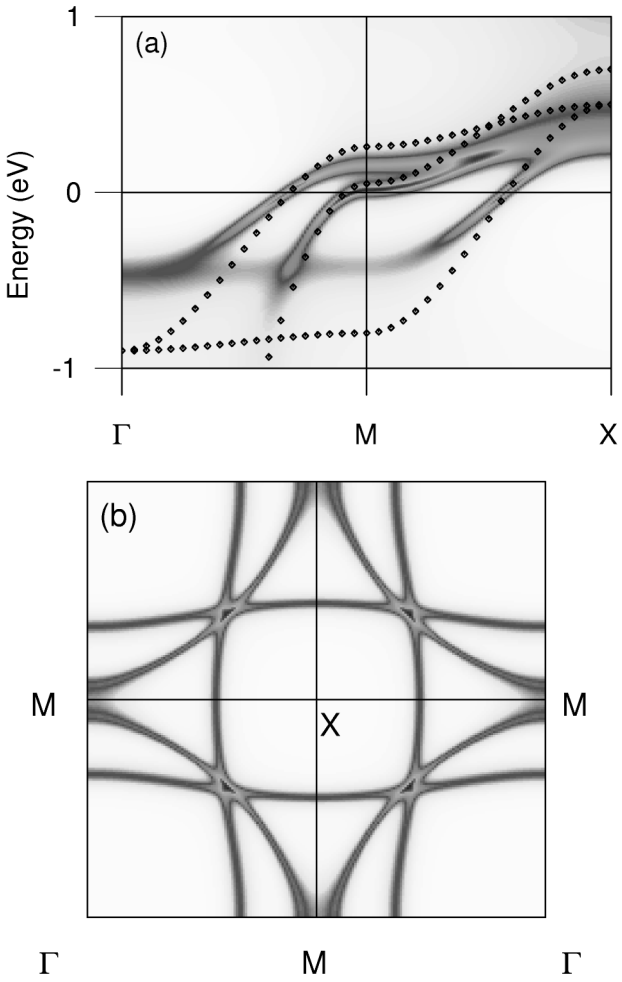

FIG. 4. (a) Quasiparticle bands along ΓM and MX derived from self-consistent second-order self-energy. Symbols: tight-binding bands. (b) Quasiparticle Fermi surface after accounting for energy broadening and resolution (see text).

related to the spectral feature observed near 2.5 eV binding energy using resonant photoemission [10]. The precise location of this satellite is difficult to determine because of the uncertainty of U and the approximate nature of our self-energy calculations.

Because of the proximity of the quasiparticle xy Van Hove critical point to the Fermi level, the imaginary part of the self-consistent self-energy exhibits a small linear contribution near E_F, indicating that the system may partially behave like a marginal Fermi liquid. In fact, in Eq. (3), it is only the first term $\sim R_{111}(\omega)$ that gives rise to a linear term if the singularity coincides with E_F. As a result of multiband effects, however, this contribution is rapidly dominated by stronger quadratic terms involving the narrow xz, yz bands. Thus, we find the marginality to be rather weak.

We finally discuss the mass renormalization derived from our quasiparticle bands. For Coulomb and exchange matrix elements in the range $U = 1.2$–1.5 eV, $J = 0.2$–0.4 eV we find $m^*/m \approx 2.1$–2.6, in agreement with photoemission estimates $m^*/m \approx 2.5$ [5], while dHvA measurements [2] and specific heat data [15] suggest a factor of 3–4.

In summary, multiband quasiparticle calculations for Sr_2RuO_4 show that the simultaneous existence of nearly one- and two-dimensional t_{2g} bands near E_F leads to a highly anisotropic self-energy of the photoemission hole state. Because of Luttinger's theorem, this anisotropy gives rise to a charge flow from the narrow xz, yz bands to the wide xy band, thereby shifting the xy Van Hove singularity very close to E_F. As a result, in the vicinity of M considerable spectral weight appears below E_F. These results might explain the controversial nature of recent photoemission data which have difficulty in determining whether or not the xy band at M is occupied.

The calculations were performed on the Cray T3e of the Forschungszentrum Jülich with grants from the John von Neumann Institute for Computing.

*Email address: a.liebsch@fz-juelich.de
†Email address: a.lichtenstein@fz-juelich.de

[1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).
[2] A. P. Mackenzie, S. R. Julian, A. J. Diver, G. J. McMullan, M. P. Ray, G. G. Lonzarich, Y. Maeno, S. Nishizaki, and T. Fujita, Phys. Rev. Lett. **76**, 3786 (1996); A. P. Mackenzie, S. R. Julian, G. G. Lonzarich, Y. Maeno, and T. Fujita, Phys. Rev. Lett. **78**, 2271 (1997).
[3] T. Yokoya, A. Chainani, T. Takahashi, H. Katayama-Yoshida, M. Kasai, and Y. Tokura, Phys. Rev. Lett. **76**, 3009 (1996); **78**, 2272 (1997); T. Yokoya, A. Chainani, T. Takahashi, H. Ding, J. C. Campuzano, H. Katayama-Yoshida, M. Kasai, and Y. Tokura, Phys. Rev. B **54**, 13 311 (1996).
[4] D. H. Lu, M. Schmidt, T. R. Cummins, S. Schuppler, F. Lichtenberg, and J. G. Bednorz, Phys. Rev. Lett. **76**, 4845 (1996).
[5] A. V. Puchkov, Z. X. Shen, T. Kimura, and Y. Tokura, Phys. Rev. B **58**, R13 322 (1998). According to these data, the intensity near M varies strongly with photon energy, suggesting that at 22 eV the xy Van Hove singularity is occupied, while above 25 eV it is unoccupied.
[6] T. Oguchi, Phys. Rev. B **51**, 1385 (1995).
[7] I. I. Mazin and D. J. Singh, Phys. Rev. Lett. **79**, 733 (1997); D. J. Singh, Phys. Rev. B **52**, 1358 (1995).
[8] A. Fang and K. Terakura (private communication).
[9] A. P. Mackenzie, S. Ikeda, Y. Maeno, T. Fujita, R. Julian, and G. G. Lonzarich, J. Phys. Soc. Jpn. **67**, 385 (1998).
[10] T. Yokoya, A. Chainani, T. Takahashi, H. Katayama-Yoshida, M. Kasai, Y. Tokura, N. Shanthi, and D. D. Sarma, Phys. Rev. B **53**, 8151 (1996).
[11] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963); J. Igarashi, P. Unger, K. Hirai, and P. Fulde, Phys. Rev. B **49**, 16 181 (1994).
[12] A. Georges, G. Kotliar, W. Kraut, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[13] M. J. Rozenberg, Phys. Rev. B **55**, R4855 (1997).
[14] M. Jarrell and J. E. Gubernatis, Phys. Rep. **269**, 133 (1996).
[15] Y. Maeno *et al.*, J. Low Temp. Phys. **105**, 1577 (1997).