

Pairing due to Spin Fluctuations in Layered Organic Superconductors

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I show that, for a κ -type organic (BEDT-TTF)₂X molecular crystal, a superconducting state with $T_c \approx 10$ K and gap nodes on the Fermi surface can be caused by short-ranged antiferromagnetic spin fluctuations. Using a two-band description for the antibonding orbitals on a BEDT-TTF dimer of the κ -type salt, and an intermediate local Coulomb repulsion between two holes on one dimer, the magnetic interaction and the superconducting gap function are determined self consistently within the fluctuation-exchange approximation. The pairing interaction is predominantly caused by interband coupling and additionally affected by spin excitations of the quasi-one-dimensional band. [S0031-9007(98)07571-1]

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Electronic mechanisms for superconductivity are of conceptual interest on their own and allow, in principle, large superconducting (SC) transition temperatures since electronic energy scales easily exceed phononic energies. In addition to the copper-oxide-based high-temperature superconductors, heavy fermion superconductors such as UPt₃ and UBe₁₃, and the ruthenate compound Sr₂RuO₄, organic superconductors are candidates for a pairing mechanism which originates in strong electronic correlations in the normal state.

The organic molecular crystals κ -(BEDT-TTF)₂X [in the following abbreviated as κ -(ET)₂X] are very anisotropic quasi-two-dimensional superconductors with transition temperatures up to about 10 K, depending on pressure and the ion X, which can, for example, be I₃, Cu[N(CN)₂]Br or Cu(SCN)₂ [1]. Shubnikov-de Haas experiments have established the existence of a well-defined Fermi surface (FS) in these materials [2,3], demonstrating the Fermi liquid character of the low energy quasiparticles. Below T_c , the low temperature ¹³C-NMR spin-lattice relaxation rate varies as T^3 [4–6], the electronic specific heat coefficient exhibits a magnetic field dependence $\gamma \propto B^{1/2}$ [7], and the thermal conductivity κ is linear in T [8]; evidences for nodes of the SC gap function on the FS. All of these results suggest that superconductivity is caused by a highly anisotropic and likely nonphononic pairing interaction. An electronic mechanism is also supported by the absence of an isotope shift of T_c due to the C=C and C—S phonon modes, as observed by ³⁴S and ¹³C=¹³C isotope substitution in the central part of the ET molecule [9].

It was pointed out earlier that many anomalous normal state properties of layered organics strongly suggest the important role of electronic correlations [10–12] and that some, but not all, of these anomalies are in striking similarity to cuprate superconductors [13]. Particularly, magnetotransport, the thermoelectric power, and the uniform magnetic susceptibility display similar behavior. Another resemblance is their proximity to an antiferromagnetic (AF) state, even though, in organics, frustration and strong

in-plane anisotropies demonstrate differences between both systems. Particularly, due to the (by now established) dominant $d_{x^2-y^2}$ order parameter component [14], high-temperature superconductivity in cuprates is believed to be dominated or entirely caused by an electronic mechanism. The spin fluctuation scenario [15,16], which predicted the $d_{x^2-y^2}$ state, is a very promising approach, because it also offers an explanation for a variety of anomalous normal state properties of cuprates. The unfrustrated AF nearest neighbor coupling and the specific shape of the FS are important prerequisites for a spin-fluctuation-induced SC state with $d_{x^2-y^2}$ symmetry in cuprates. In contrast, in organics, the magnetic coupling is frustrated, due to the underlying anisotropic triangular lattice [13]. In addition, their FS consists of two disconnected pieces [2,3]. Therefore, it is not at all obvious whether, despite these numerous similarities to cuprates, spin fluctuations can bring about superconductivity in the organics.

In this paper, I show that spin fluctuations can cause superconductivity with $T_c \approx 10$ –15 K in κ -type organic molecular crystals [17] and discuss similarities between the interband coupling and the *hot spot* scenario of cuprates [15,18]. Gap nodes on the FS, accompanied by changes in sign of the order parameter, result because of zone boundary interband pairing combined with an intraband coupling of a quasi-one-dimensional (quasi-1D) band. This is in agreement with NMR and specific heat measurements, and should be observable in a corresponding phase shift experiment. Furthermore, the strong interband pairing interaction causes an opposite sign of the gap functions of the two bands.

Within a given conducting layer, the unit cell of κ -(ET)₂X is occupied with six electrons in the outer electronic shells and consists of four ET molecules, which can be considered as single electronic degrees of freedom [19]. The four molecules are arranged in two dimers (see Fig. 1a). Because of the large intradimer transfer integral, $t_1 \approx 250$ meV, the two bonding bands are completely occupied and shifted to binding energies $\sim 2t_1$ below the Fermi energy. Only the two remaining antibonding bands

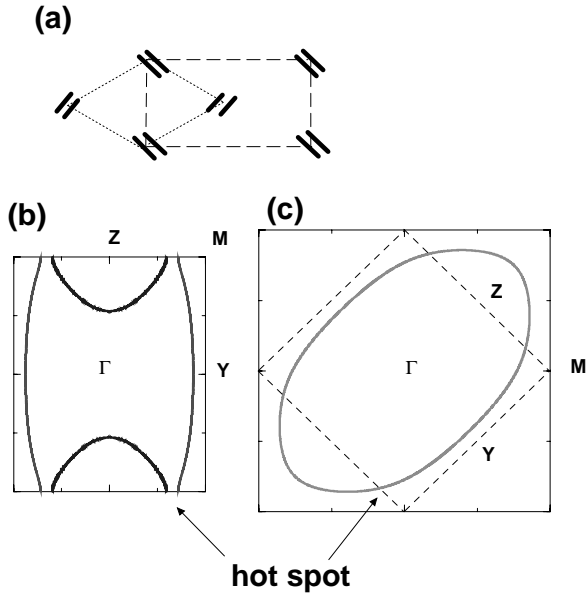


FIG. 1. (a) Spatial arrangement of the ET molecules within the planes. The two dimer types are indicated by the different tilting of the molecule pairs, which are, after dimerization, considered as a single electronic degree of freedom. The dashed (dotted) lines indicate the unit cell for $t_3 \neq t_{3'}$ ($t_3 = t_{3'}$). (b) Fermi surface for the case $t_3 \neq t_{3'}$, consisting of a quasi-1D band and a hole pocket closed around the Z point. (c) Fermi surface for the case $t_3 = t_{3'}$. Note that the *hot spots* due to nearest neighbor AF correlations correspond to the gaps between both Fermi surface parts in (b).

cross the FS; those are half filled with the remaining two electrons.

In what follows, I consider only the two antibonding bands near the Fermi surface (within a hole picture) and neglect the bonding bands. Because of the strong intramolecular Coulomb repulsion ($U_{ET} \geq 1$ eV), a doubly occupied dimer will likely distribute the two holes on both molecules of the dimer, causing an effective correlation energy $U \sim 2t_1$ determined by the bonding-antibonding band splitting [13]. This leads to the following two-band Hubbard Hamiltonian:

$$H = \sum_{ij,l,\sigma} t_{ij} c_{il\sigma}^\dagger c_{jl\sigma} + U \sum_{i,l} n_{il\uparrow} n_{il\downarrow} + \sum_{ij,\sigma} \tilde{t}_{ij} (c_{i1\sigma}^\dagger c_{j2\sigma} + c_{j2\sigma}^\dagger c_{i1\sigma}). \quad (1)$$

Here, $c_{il\sigma}^\dagger$ is the creation operator of a hole with spin σ in the antibonding band of the l th dimer ($l \in \{1, 2\}$) in the i th unit cell and $n_{il\sigma} = c_{il\sigma}^\dagger c_{il\sigma}$. t_{ij} and \tilde{t}_{ij} are interdimer hopping elements between dimers of the same and of different types, respectively. Their Fourier transforms $t_{\mathbf{k}}$ and $\tilde{t}_{\mathbf{k}}$ with $\mathbf{k} = (k_y, k_z)$ determine the band structure of the two bands $\varepsilon_{\mathbf{k},\pm} = t_{\mathbf{k}} \pm \tilde{t}_{\mathbf{k}}$. Various different tight binding parametrizations have been proposed for $t_{\mathbf{k}}$ and $\tilde{t}_{\mathbf{k}}$ [2,19–21]. I will use the disper-

sion relation $t_{\mathbf{k}} = 2t_2 \cos(k_y)$ and $\tilde{t}_{\mathbf{k}} = 2 \cos(k_y/2) \times \sqrt{t_3^2 + t_{3'}^2 + 2t_3 t_{3'} \cos(k_z)}$ [2,21], which can be derived from a four-band model up to leading order in t_2/t_1 . Because of the nonsymmetrical position of the dimers and the ET molecule structure itself, the three hopping elements are slightly different. The FS, for $t_2 = 45$ meV, $t_3 = 60$ meV, and $t_{3'} = 65$ meV, shown in Fig. 1b, reproduces de Haas-van Alphen measurements [3] and electronic structure calculations [19]. Note, the two pieces of the FS are disconnected since $t_3 \neq t_{3'}$.

For the investigation of an electronic pairing state, one has to determine the momentum and frequency dependence of the pairing interaction which is responsible for the magnitude, $|\Delta_{ll'}^{ij}|$, of the coordinate space components of the gap function $\Delta_{ll'}^{ij} \propto \langle c_{il\uparrow} c_{j'l\downarrow} \rangle$ and the relative phase relations which the $\Delta_{ll'}^{ij}$ establish. The latter effect is determined by the maximum gain of condensation energy on the FS. In order to have a quantitative account for this interplay of magnetic correlations, FS shape, and interband and intraband coupling, I use a self-consistent summation of bubble and ladder diagrams (fluctuation-exchange approximation [22,23]) within the Nambu-Gorkov description of the SC state. Both the pairing interaction and the SC gap function will be determined self-consistently. Whether superconductivity occurs and whether the gap function possesses nodes on the FS will therefore be the results of our calculation.

The fluctuation-exchange approximation has been successfully used for the investigation of superconductivity in one band models relevant for high-temperature superconductors [22–24]. For completeness, I give the set of equations for the two-band Hamiltonian, Eq. (1), within the SC state. The effective interactions of the system,

$$V^\pm(q) = \frac{3U^2}{2} \left\{ [1 - U\chi^s(q)]^{-1} - \frac{1}{3} \right\} \chi^s(q) \pm \frac{U^2}{2} \{ [1 + U\chi^c(q)]^{-1} - 1 \} \chi^c(q), \quad (2)$$

are (2×2) matrices in the dimer representation with particle-hole bubble $\chi_{ll'}^{s(c)}(q) = -\sum_k G_{ll'}(k) G_{l'l}(k+q) + (-)F_{ll'}(k) F_{l'l}(k+q)$ for spin- and charge-type excitations. Here $G_{ll'}(k)$ and $F_{ll'}(k)$ are the normal and anomalous Green's functions with $q = (\mathbf{q}, i\nu_n)$, $k = (\mathbf{k}, i\omega_n)$ as well as $\sum_k = T/N \sum_{\mathbf{k}, n}$. \mathbf{k}, \mathbf{q} are the two-dimensional wave vectors, and the Matsubara frequencies are given by $\omega_n = (2n+1)\pi T$ for fermions and $\nu_n = 2n\pi T$ for bosons. T is the temperature and N is the number of unit cells. From the effective interaction, Eq. (2), in the dimer representation, one can obtain the intraband and interband interactions $V_{\lambda,\lambda'}^\pm(q)$ with $\lambda, \lambda' \in \{+, -\}$. The self energy in Nambu representation is assumed to be diagonal in the band representation:

$$\hat{\Sigma}_\lambda(k) = Y_\lambda(k) \hat{\tau}^0 + X_\lambda(k) \hat{\tau}^3 + \Phi_\lambda(k) \hat{\tau}^1, \quad (3)$$

Here, $Y_\lambda(k) \equiv i\omega_n[1 - Z_\lambda(k)]$ and $X_\lambda(k)$ are the diagonal and $\Phi_\lambda(k)$ the off-diagonal components of the self-energy in Nambu representation, respectively, and can be determined from the Eliashberg equations,

$$Y_\lambda(k) = \sum_{k',\lambda'} V_{\lambda,\lambda'}^+(k - k') i\omega_n Z_{\lambda'}(k') / D_{\lambda'}(k'),$$

$$X_\lambda(k) = \sum_{k',\lambda'} V_{\lambda,\lambda'}^+(k - k') [\varepsilon_{k',\lambda'} + X_{\lambda'}(k')] / D_{\lambda'}(k'), \quad (4)$$

$$\Phi_\lambda(k) = \sum_{k',\lambda'} [V_{\lambda,\lambda'}^-(k - k') + U] \Phi_{\lambda'}(k') / D_{\lambda'}(k'),$$

with denominator $D_\lambda(k) = [i\omega_n Z_\lambda(k)]^2 - [\varepsilon_{k,\lambda} + X_\lambda(k)]^2 - \Phi_\lambda(k)^2$. The off-diagonal self-energy, which signals superconductivity, determines the gap function $\Delta_\lambda(k) = \Phi_\lambda(k) / Z_\lambda(k)$. After analytical continuation to the real axis, $i\omega_n \rightarrow \omega + i0^+$, this set of coupled equations is solved self-consistently using the numerical framework described in Ref. [25].

In Fig. 1a, we show the unit cell, and in Fig. 1b, the corresponding FS, determined by $\varepsilon_{\mathbf{k},\pm}$. The FS segments of the two bands appear as one quasi-1D and one hole pocket part, as seen in magneto-oscillation experiments [2,3]. This FS generates $2k_F$ intraband transitions within the quasi-1D band. In a real space picture, this corresponds to a coupling between dimers of the same type. In addition, we expect strong couplings $J_{3,3'} \propto t_{3,3'}^2 / U$ between dimers of different types. The numerical analysis of the above set of equations shows that this latter effect, which causes a magnetic interband coupling, dominates. Correspondingly, the interband effective interactions $V_{\mathbf{q}+}^\pm(\omega)$ are large compared to $V_{\mathbf{q}++}^\pm(\omega) = V_{\mathbf{q}-}^\pm(\omega)$ and peaked at $\mathbf{q} = (\pm\pi, 0)$. This result is shown in Fig. 2,

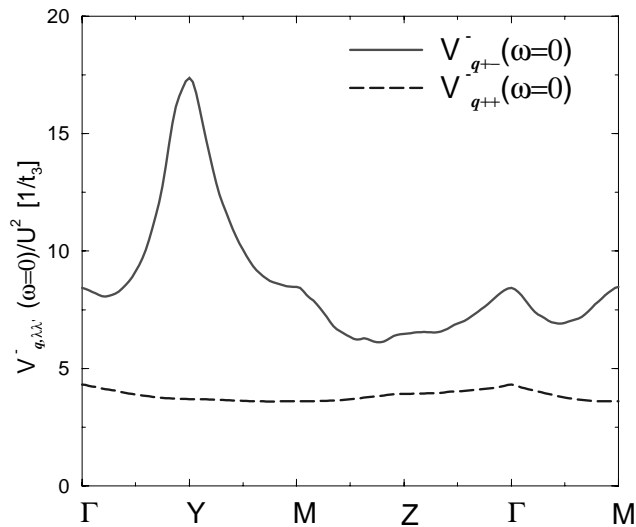


FIG. 2. Effective pairing interaction for intraband and interband excitations along the high symmetry lines of the Brillouin zone. Note the pronounced peak at $\mathbf{q} = (\pi, 0)$ for interband excitations.

where we plot $V_{\mathbf{q}\lambda\lambda'}^-(\omega = 0)$ along the high symmetry lines of the Brillouin zone (BZ). Because of this strong interband coupling, we expect a relative sign -1 for the gap functions of the two bands: $\Delta_{\mathbf{k},+} \approx -\Delta_{\mathbf{k},-}$. Furthermore, the pronounced anisotropy of the pairing interaction, peaked at $\mathbf{q} = (\pm\pi, 0)$, will cause a substantial momentum dependence of $\Delta_{\mathbf{k},\pm}$.

Our numerical results for the anomalous self-energy $\Phi_{\mathbf{k},\pm}(\omega = 0) \propto \Delta_{\mathbf{k},\pm}$ are shown in Fig. 3. We find a stable SC solution, caused by AF spin fluctuations at a temperature $T = 8$ K which exhibits zeroth of the gap function along the lines $k_{y,z} = 0$. The leading harmonics of the gap function are given by $\Delta_{\mathbf{k},\pm} \approx \Delta_{\pm}^0 \sin(k_y/2) \sin(k_z/2)$ with $\Delta_+^0 = -0.9$ meV and $\Delta_-^0 = 1.5$ meV. As shown in Fig. 1c, this gives gap nodes for both pieces of the FS. The symmetry of this superconducting state is d_{yz} which, in addition, is out of phase between the two parts of the FS. The transition temperature $T_c = 13$ K is in fair agreement with the experiment. Because of the strong quasiparticle scattering rate for larger values of U , T_c does not exceed values at about 20 K.

The physical origin of this pairing state and the close resemblance to the $d_{x^2-y^2}$ state in cuprates can be understood if, for illustrating purposes, one makes the assumption $t_3 = t_{3'}$ for the hopping elements between different dimer types. Now, the two dimer types, which differ in their orientation of the molecule pairs, are indistinguishable and the unit cell reduces to that indicated by dotted lines in Fig. 1a. Assuming, furthermore, that the dimers are arranged on a square lattice, the BZ is doubled and rotated by $\pi/4$. The

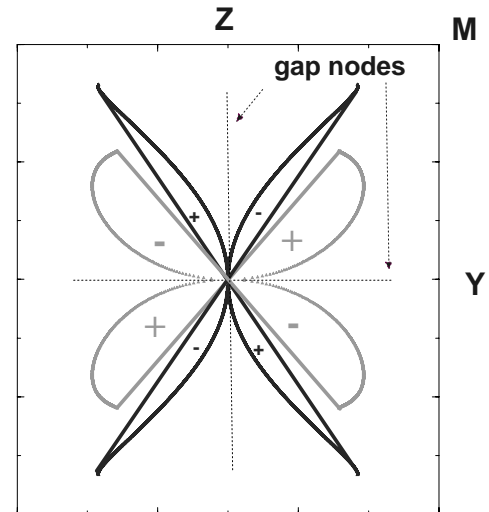


FIG. 3. Polar plot of the superconducting gap functions $\Delta_{\mathbf{k},\pm}$ of the two bands along the FS. For a given angle $\tan^{-1}(k_z^F/k_y^F)$ with Fermi vector (k_y^F, k_z^F) , the amplitude of the gap corresponds to the distance from the origin. Gap nodes occur along the k_y and k_z axes. The suppressed gap close to the diagonal is due to the absence of a FS. If $t_3 = t_{3'}$ this region vanishes with equal gap amplitude at the meeting point of the two FS parts.

resulting FS is shown in Fig. 1c. One easily recognizes that the two branches of the FS of Fig. 1b correspond, after downfolding into the reduced BZ, to states separated by the dashed line in Fig. 1c. Since in coordinate space the dominating AF coupling is between nearest neighbors, it causes peaks in the magnetic susceptibility at about $(\pm\pi, \pm\pi)$ of the extended BZ. A quantitative calculation shows that the additional anisotropy due to the hopping element t_2 causes the peaks at $\pm(\pi, \pi)$ to differ from those at $\pm(\pi, -\pi)$. Nevertheless, $(\pm\pi, \pm\pi)$ are the dominating momentum transfers causing anomalies for *hot* quasiparticles, located on FS segments close to the corresponding magnetic zone boundary (dashed line in Fig. 1c) [18,26], which lead to the interband coupling in the original BZ of Fig. 1b. On the other hand, as discussed in detail in Refs. [15,16], a momentum transfer $(\pm\pi, \pm\pi)$ causes a superconducting state with gap function $\Delta_{\mathbf{k}} \propto \cos k_y - \cos k_z$. Rotation by $\pi/4$ and downfolding into the reduced BZ of Fig. 1b yield $\Delta_{\mathbf{k},\pm} \propto \pm \sin(k_y/2) \sin(k_z/2)$ which covers the general behavior of the results presented in Fig. 3. Thus, subject to the modifications brought about by the gap between the two branches of the FS and the additional anisotropy of the underlying lattice, the origin of the pairing state in cuprates and organics is very similar. Because of the important role played by *hot* momentum states for various normal state anomalies of cuprates [18,26], it is tempting to conclude that the occurrence of two distinct classes of quasiparticles, *hot* and *cold*, depending on the strength of the effective interaction are essential for the unconventional behavior in organics as well.

In conclusion, I have shown that spin fluctuations are a promising candidate for the pairing interaction of the superconducting state of organic molecular crystals. I find a transition at 13 K to a superconducting state, in which the calculated occurrence of nodes on the FS is in agreement with various experimental observations. Furthermore, within the spin-fluctuation model, a close similarity of the origin of this pairing symmetry to the one in cuprate superconductors was demonstrated. Nevertheless, it should be noted that the self-consistent weak-coupling approach, used in the present paper, does not cover strong-coupling effects such as the formation of a frustration-induced spin liquid state nor does it provide the desirable quantitative description of the low-frequency spin dynamics as reached in cuprates [15]; rather it is only expected to give qualitatively correct information about the occurrence and symmetry of a SC state.

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- [1] M. Lang, *Supercond. Rev.* **2**, 1 (1996).
- [2] J. Caulfield *et al.*, *J. Phys. Condens. Matter* **6**, 2911 (1994).
- [3] C.H. Mielke *et al.*, *Phys. Rev. B* **56**, R4309 (1997).
- [4] S.M. De Soto, C.P. Slichter, A.M. Kini, H.H. Wang, U. Geiser, and J.M. Williams, *Phys. Rev. B* **52**, 10364 (1995).
- [5] H. Mayaffre *et al.*, *Phys. Rev. Lett.* **75**, 4122 (1995).
- [6] K. Kanoda *et al.*, *Phys. Rev. B* **54**, 76 (1996).
- [7] Y. Nakazawa and K. Kanoda, *Phys. Rev. B* **55**, R8670 (1997).
- [8] S. Belin, K. Behnia, and A. Deluzet, *cond-mat/9805354*.
- [9] K. Kanoda and Kotai Buzuri, *Solid State Phys.* [in Japanese] **30**, 240 (1995).
- [10] L.N. Bulaevskii, *Adv. Phys.* **37**, 443 (1988).
- [11] H. Kino and H. Fukuyama, *J. Phys. Soc. Jpn.* **65**, 2158 (1996).
- [12] K. Kanoda, *Physica (Amsterdam)* **282C**, 299 (1997).
- [13] R.H. McKenzie, *Science* **278**, 820 (1997); *cond-mat/9802198*.
- [14] D.J. Van Harlingen, *Rev. Mod. Phys.* **67**, 515 (1995).
- [15] D. Pines, *Z. Phys. B* **103**, 129 (1997); *The Gap Symmetry and Fluctuations in High- T_c Superconductors*, edited by J. Bok and G. Deutscher NATO ASI (Plenum, New York, 1998).
- [16] D.J. Scalapino, *Phys. Rep.* **250**, 329 (1995).
- [17] Within the spin-fluctuation model, superconductivity can be understood in the α and β configuration of $(\text{ET})_2\text{X}$ as well. This is determined by the shape of the FS and the strength of the interaction. The FS of the β -type configuration is very similar to the one shown in Fig. 1c. The FS of the α -type materials, rotated by 90° and plotted in a repeated zone representation is again rather similar to that of the κ -type configuration. However, the more pronounced 1D character of the α -type configuration may also favor a $\cos(k_y)$ intraband pairing due to spin fluctuations.
- [18] R. Hlubina and T.M. Rice, *Phys. Rev. B* **51**, 9253 (1995); *ibid.* **52**, 13043 (1995); B.P. Stojkovic *et al.*; and D. Pines, *Phys. Rev. Lett.* **76**, 811 (1996); *Phys. Rev. B* **55**, 8576 (1997).
- [19] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, *Phys. Rev. B* **38**, 938 (1988).
- [20] M. Tamura *et al.*, *J. Phys. Soc. Jpn.* **60**, 3861 (1991).
- [21] V. Ivanov *et al.*, *Physica (Amsterdam)* **275C**, 26 (1997).
- [22] C.H. Pao and N.E. Bickers, *Phys. Rev. Lett.* **72**, 1870 (1994).
- [23] P. Monthoux and D.J. Scalapino, *Phys. Rev. Lett.* **72**, 1874 (1994).
- [24] S. Grabowski, M. Langer, J. Schmalian, and K.H. Bennemann, *Europhys. Lett.* **34**, 219 (1996).
- [25] J. Schmalian, M. Langer, S. Grabowski, and K.H. Bennemann, *Comput. Phys. Commun.* **93**, 141 (1996); the calculations are done on a 64×64 lattice in momentum space and using 2^{12} frequency points in the interval $[-30t_3, 30t_3]$.
- [26] J. Schmalian, D. Pines, and B. Stojković, *Phys. Rev. Lett.* **80**, 3839 (1998).