Spin-density-wave instabilities for imperfectly nested Fermi surfaces: Application to BEDT-TTF salts

Miguel Gusmão* and Timothy Ziman†
Laboratoire de Physique Quantique, Université Paul Sabatier, CNRS (URA 505), 118 route de Narbonne, 31062 Toulouse, France
(Received 12 March 1996)

We discuss criteria for determining the optimal nesting vector from the maximum of the zero-field susceptibility for imperfectly nested Fermi surfaces. In particular, we present results for some of the bis(ethylenedithio) tetrathiafulvalene charge-transfer salts, a family of quasi-two-dimensional organic conductors. The criteria proposed gives better nesting than the previous criteria that has been applied to the tetramethyltetraselenafulvalene family, in which the nesting vector translates a point of inflection on the Fermi surface. We discuss the nesting vectors deduced, and consequences for Fermi-surface reconstruction and low-temperature behavior. [S0163-1829(96)01648-7]

I. INTRODUCTION

In the search for solids with interesting conducting properties one of the most fruitful approaches has been the synthesis and study of organic charge-transfer salts.[1] Such salts tend to have highly anisotropic conducting properties, since the molecular orbitals responsible for conduction are anisotropic. The first class extensively studied, tetrathiafulvalene-tetracyano-*p*-quinodimethane (TTF-TCNQ),[2] has electronic properties determined by a quasi-one-dimensional herringbone structure. The properties of low-dimensional metals are dominated by instabilities toward formation of spin- or charge-density waves that compete with superconducting instabilities. To improve the conducting properties at low temperature, attempts were made to develop structures with higher dimensionality in order to avoid such instabilities. The family of Bechgaard salts[3] $(TMTSF)_2X$ retain open Fermi surfaces but present larger transverse couplings. Some of the compounds are superconducting, and there have been extensive studies of the competition between density-wave and superconducting instabilities as a function of applied pressure and magnetic field.[4,5]

Another class of metallic charge-transfer salts is based on the molecule known as BEDT-TTF or ET (Ref. 6) [bisethylenedithio(tetrathiafulvalene)]. Typically, salts based on this molecule present a stacked-layer structure. Observations of Shubnikov–de Haas and de Haas–van Alphen oscillations have given information on the Fermi-surface properties which are in good agreement with band-structure calculations based on the overlap of the molecular π orbitals. Such extended Hückel calculations[7–9] predict, in some cases such as the α phases of $(BEDT\text{-}TTF)_2X$, Fermi surfaces which have an open electron part and a closed holelike pocket. Frequently the open part is referred to as *quasi-one-dimensional*, as it leads to open orbits in an applied magnetic field. In fact the Fermi surfaces calculated are not only far from parallel but depart substantially from the sinusoidal form which comes from weakly coupled chains. Nevertheless, from the geometry it is clear that there is an approximate nesting which will give enhanced charge or spin susceptibilities. Consistent with this, some of the compounds suffer transitions to magnetically ordered states at low temperatures, while others become superconducting. So far, to our knowledge, there has not been a systematic study to explain what determines the low-temperature behavior, and it is part of the aim of this paper to explore this issue. We will be mostly concerned with the behavior in zero external magnetic field, but we will discuss its relevance to field-dependent phenomena, since studies in finite magnetic field give the most direct information on the low-temperature electronic structure.

II. NESTING CRITERIA

Within a Stoner-type theory of electronic instability, the **Q** vector at low temperature is determined by the maximum of the noninteracting susceptibility

$$\chi^0(\mathbf{Q}) = -\frac{2}{\mathcal{V}} \sum_\alpha \int \frac{n(\epsilon^\alpha_{\mathbf{k}+\mathbf{Q}}) - n(\epsilon^\alpha_{\mathbf{k}})}{\epsilon^\alpha_{\mathbf{k}+\mathbf{Q}} - \epsilon^\alpha_{\mathbf{k}}} d\mathbf{k}, \tag{1}$$

where $\mathcal{V}$ is the volume of the first Brillouin zone, $n(\epsilon)$ is the Fermi-Dirac distribution function (which becomes a step function at zero temperature), and $\epsilon^\alpha(\mathbf{k})$ is the dispersion relation of the band α. In BEDT-TTF salts the susceptibility is summed over the contributions of two partially filled bands.

For a model with perfectly planar energy surfaces in **k** space, where the planes are taken to be parallel in the x direction, $\epsilon_{\mathbf{k}} = \epsilon(k_x)$, with $\epsilon(k_F) = \epsilon_F$. Then there is a degeneracy, in that for any vector $\mathbf{Q} = (2k_F, Q_y, Q_z)$ we have $\epsilon_{\mathbf{k}+\mathbf{Q}} = \epsilon_{\mathbf{k}}$ for *all* $\mathbf{k} = (-k_F, k_y, k_z)$ on the Fermi surface. Integration perpendicular to the Fermi surface in Eq. (1) gives a logarithmically divergent contribution from the lower limit of the integrand in

$$\int_{k_F}^{k_u} \frac{1}{v_F(k_x - k_F) + O((k_x - k_F)^2)} dk_x, \tag{2}$$

where k_u is an upper cutoff and $v_F = \partial\epsilon(k_x)/\partial k_x|_{k_x = k_F}$.

From now on we will refer to two-dimensional vectors **k**, both for simplicity of notation and because we are primarily interested in quasi-two-dimensional systems. If we take a two-dimensional model with dispersion $\epsilon(\mathbf{k}) = v_F(|k_x| - k_F) - 2t_b \cos k_y$, then the above degeneracy is broken, since only the vector $(2k_F, \pi)$ gives perfect nesting, and the

susceptibility remains infinite for this value of **Q** only. Montambaux and co-workers[4,5] considered the model of Gor'kov and Lebed',[10] in which a small second harmonic is added in the y direction: $\epsilon(\mathbf{k})=v_F(|k_x|-k_F)-2t_b\cos k_y-2t_b'\cos(2k_y)$. This second harmonic does two things: it reduces the susceptibility at $(2k_F,\pi)$ to a finite value, and moves the maximum susceptibility to a different **Q** which is incommensurate in both coordinates. This agrees with an argument due to Jafarey[11] that the nesting vector is determined by the point of inflection of the Fermi surface.

For a general surface (or line in two-dimensional cases) the denominator in Eq. (1) for a given **Q** vanishes only at a point or points, so that the logarithmic singularity from integration perpendicular to the Fermi surface occurs at discrete points. If we now integrate in the tangential direction, the singularity (2) contributes a finite amount. How much it contributes depends on how good the nesting is locally, that is to say, how fast the denominator increases from zero. We will denote by k_1 and k_2 the components of the wave vector normal and tangential to the Fermi surface measured from a point at which there is nesting, i.e., where the denominator in Eq. (1) vanishes. These directions will in general be rotated with respect to x and y. We first integrate in the normal direction,

$$\int_0^{k_u}\frac{1}{r(k_2)+v_Fk_1+\cdots}dk_1. \tag{3}$$

The function $r(k_2)$ cuts off the logarithmic divergence in Eq. (3). Taking the leading term in $r(k_2)=a_p{k_2}^p$, and introducing a cutoff k_{2co}, the second integration makes a singular but finite contribution

$$\int_0^{k_{2co}}\ln\left(\frac{1}{|a_p{k_2}^p|}\right)dk_2=k_{2co}\ln\left(\frac{e^p}{|a_pk_{2co}^p|}\right). \tag{4}$$

If all else is equal this contribution increases with p, the degree of nesting.

Let us now consider a model in which the Fermi surface has two open branches. If the wave vector is such that a point on one branch is translated to a point on the other, with parallel tangent, the nesting makes a contribution with $p=2$. This is associated with a Kohn anomaly, i.e., a singular dependence of the susceptibility as a function of wave vector. For surfaces displaying a center of inversion, this tangential condition can be satisfied starting with any point on the open surface: it suffices to translate through the origin. An example of this is shown in Fig. 1. If we choose a point of inflection on the Fermi surface as the starting point, however, the difference is of higher order $(p=4)$. Thus it is quite likely that it will have a larger integral. This cannot guarantee an absolute maximum, since Eq. (4) is finite; but it is plausible, and indeed was numerically verified for the case of a weak second harmonic commented upon above. It is tempting then to apply this geometric criterion to more general cases. There are other possibilities, however. For instance, the criterion for quadratic nesting is not exclusive to translations through the origin. Let us define the two branches of an open Fermi surface by the functions $k_x=f_-(k_y)$ for the branch $k_x<0$ and $k_x=f_+(k_y)$ for the branch $k_x>0$ (see Fig. 1). If there is inversion symmetry the functions are related by

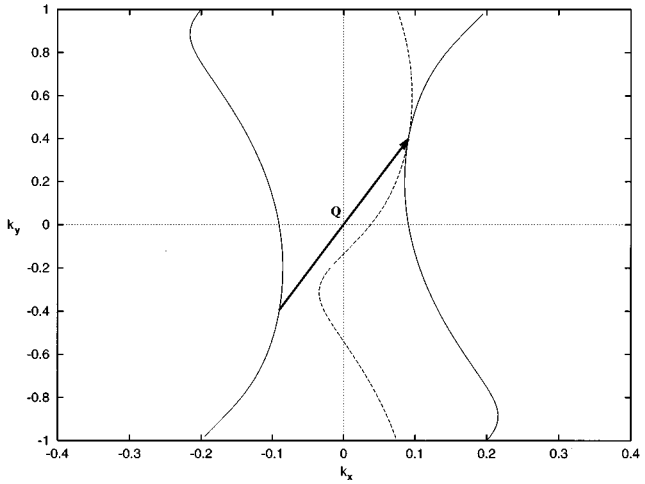

FIG. 1. Nesting vector determined from taking a point on one branch of the Fermi surface to the other passing through the origin.

$f_+(y)=-f_-(-y)$. A general translation (Q_x,Q_y) from a point on the left-hand open Fermi surface $[f_-(k_y^0),k_y^0]$ to another on the right-hand branch with a parallel tangent gives two equations:

$$\begin{aligned}Q_x+f_-(k_y^0)&=f_+(k_y^0+Q_y),\\ f_-'(k_y^0)&=f_+'(k_y^0+Q_y).\end{aligned} \tag{5}$$

Using inversion symmetry, this second equation can be written as

$$f_-'(k_y^0)=f_-'(-k_y^0-Q_y), \tag{6}$$

which clearly gives the parametric solution to Eq. (5):

$$\begin{aligned}Q_y&=-2k_y^0,\\ Q_x&=-2f_-(k_y^0),\end{aligned} \tag{7}$$

which corresponds to inversion through the origin as previously described. Depending on k_y^0 there may be other solutions which must be found numerically for a general curve. If we take the particular case

$$f_-(k_y)=-k_F-2t_b(\cos k_y+r\cos(2k_y)), \tag{8}$$

which corresponds to the model of Gor'kov and Lebed' commented upon above, with $r\equiv t_b'/t_b$, we have the solution

$$k_y^0=-\frac{Q_y}{2}+\arccos\left[-\frac{\cos\left(\frac{Q_y}{2}\right)}{4r\cos(Q_y)}\right], \tag{9}$$

provided

$$\left|\frac{\cos\left(\frac{Q_y}{2}\right)}{4r\cos(Q_y)}\right|\leqslant 1. \tag{10}$$

This was studied[4] for the case of $(TMTSF)_2ClO_4$ for $r=\frac{1}{30}$. The extra solution defines other line segments in the space of (Q_x,Q_y) where the susceptibility has a cusp, and may define local or global maxima. Montambaux[4] showed

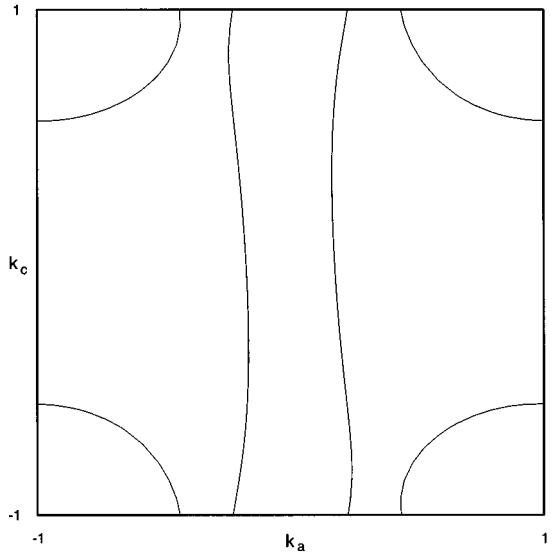

FIG. 2. Fermi surface of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ for the parameters given by Mori *et al.*[7] The **k** vectors are in units of $(\pi/a, \pi/c)$.

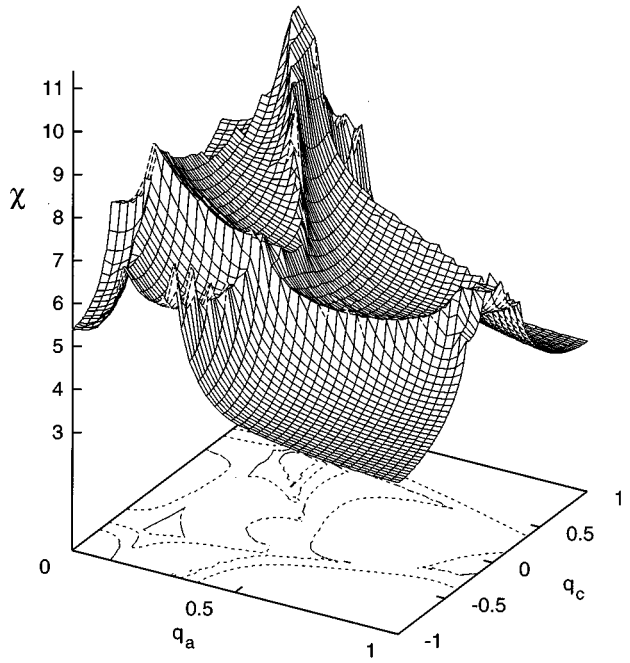

FIG. 3. Susceptibility of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ as a function of wave vector.

that the additional line meets the lines defined by Eq. (7) at the points of inflection, so that the quartic nesting may be considered as coming from the fusion of two quadratic nestings. It has been considered that this criterion of quartic nesting associated with the point of inflection may be generally applicable.

We now come to another possible criterion based on purely geometric considerations, that is to say the shape of the Fermi surface, and not the form of the whole energy surface. This comes from the observation that there is at least one other special point in the space of nesting vectors which, rather than a quartic nesting, gives *two simultaneous* quadratic divergences, coming from the touching of two *distinct* points on the open Fermi surfaces. From the form of the singular criterion (4) two singularities with $p=2$ can easily contribute as much as a single with $p=4$. Such a point must occur since Q_x passes *twice* across the first Brillouin zone as k_y^0 varies between 0 and 2π in the parametric equations (5). The two lines so defined must intersect by periodicity. At this point the **Q** vectors come from k_y^0 and $k_y^0+\pi$, so the condition on k_y^0 is that $f_-(k_y^0)=f_-(k_y^0+\pi)$. Geometrically, the contours of $\epsilon(\mathbf{k}+\mathbf{Q})$ *touch* those of $\epsilon(\mathbf{k})$ at two points. In the model given above (with a second harmonic) this occurs at $(2k_F, \pi)$ since $f_-(-\pi/2)=f_-(\pi/2)$. In that case, for the parameters appropriate to TMTSF, this nesting was worse by the criteria of having larger area and smaller susceptibility, at least at zero temperature and field. For other compounds the vector is not necessarily at the zone boundary, but can be considered a generalization of that nesting to more general forms of the open Fermi surface. It must be considered a possibility for nesting, and in fact we will see that there are cases in which it is better than the point of inflection.

III. NESTING IN THE ALPHA PHASE OF BEDT-TTF SALTS

As an illustration of these ideas, and to apply to an interesting case, we turn to a model which is used to interpret data in the family of compounds α-(BEDT-TTF)$_2X$Hg(SCN)$_4$ (X=K, NH$_4$, Rb, and Tl).[7,12] As already mentioned, this material is quasi-two-dimensional, with a ratio of anisotropy in and out of the plane[13] typically 10^3. The electronic properties in the plane are described by an anisotropic tight-binding model which differs from that of a square lattice by addition of next-nearest-neighbor hopping terms. There are four molecules per unit cell, and the overlap parameters for X=K have been calculated by Mori *et al.*[7] by the extended Hückel method. There have been recent recalculations of the tight-binding parameters by Ducasse and Fritsch,[8] and by Rousseau *et al.*[11] including other compounds of the family. These parameters are rather different, in part because there has been refinement of the structures, and in part because the values of the overlaps are sensitive to the basis set.[8] The total electron filling corresponds to three full bands. As the third and fourth bands overlap in energy, the third has a hole pocket with a closed Fermi surface, while the fourth presents open orbits. In Fig. 2 we show the Fermi surface for the potassium compound, calculated with the parameters obtained by Mori *et al.*[7]

In order to calculate the noninteracting susceptibility we evaluate the integral in Eq. (1) numerically, and sum over the two surfaces. In Fig. 3 we show the **Q**-dependent susceptibility for the parameters corresponding to the potassium compound. Here we used the parameters calculated by Ducasse and Fritsch,[8] but the results are qualitatively similar for all sets of parameters. The obvious features are lines of cusps that correspond to nesting vectors of the open Fermi surfaces, but also other weaker cusps that correspond to displaced hole pockets that just touch. The maximum susceptibility corresponds to that **Q** vector where the two cusp lines from the open branches meet. This is a case in which one has two simultaneous quadratic nestings, as discussed in Sec. II.

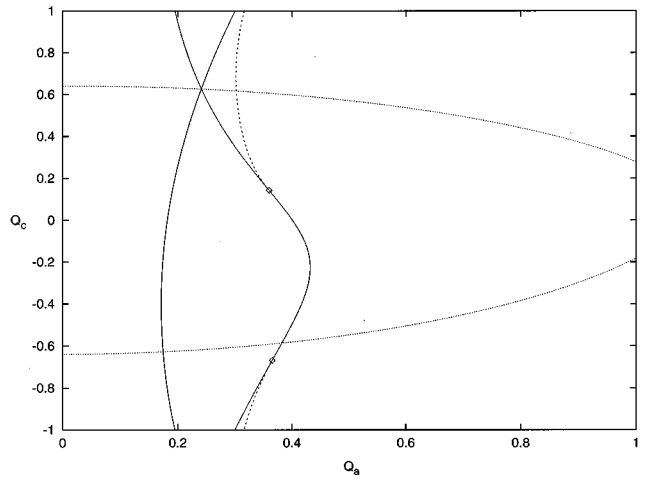

FIG. 4. The lines of cusps in the **Q**-dependent susceptibility of α-(BEDT-TTF)$_2$KHg(SCN)$_4$. The continuous (dashed) lines give the points of quadratic nesting for the open branches of the Fermi surface with the nesting points on each branch related (not related) by inversion through the origin. The dotted lines correspond to displaced hole pockets that touch the original ones. The squares indicate the nesting vectors for the points of inflection of the open Fermi surfaces.

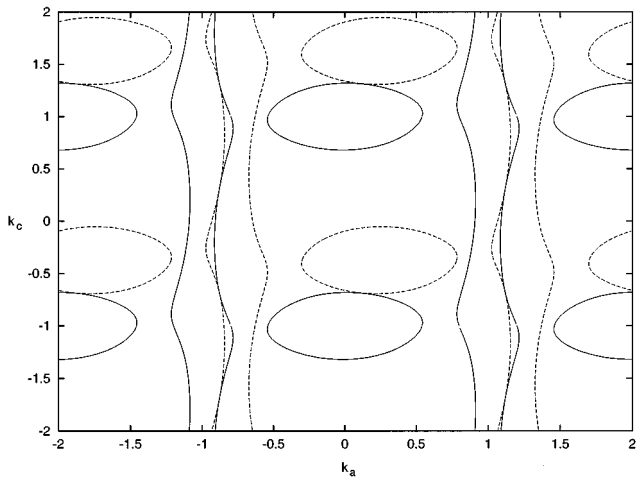

FIG. 5. Original (continuous lines) and displaced (dashed lines) Fermi surfaces of the potassium compound for the best nesting vector. Notice the small pockets resulting from imperfect nesting of the open branches, and the fact that the closed hole pockets just touch.

This **Q** vector is quite distinct from that given by the point of inflection, and the susceptibility is distinctly higher. In Fig. 4 we show the lines given by the solutions of Eq. (7) for the Fermi surface of the BEDT-TTF potassium compound, both for the open and closed branches. Comparing with Fig. 3, one sees that these lines coincide with the cusps of the susceptibility. We note that the point where the cusp lines corresponding to the open branches cross is also a point on the line of singularities coming from the hole pocket nesting condition. This fact, which may be assumed accidental, implies that even though the predicted nesting vector depends primarily on the geometry of the *open* Fermi surfaces, it gives rise to near nesting of the closed part as well. Partly because of this the contribution to the total susceptibility (10 eV^{-1}) that comes from the closed surface (3.5 eV^{-1}) is comparable to that coming from the open part (6.5 eV^{-1}). Similarly for the other compounds the contributions from both surfaces must be included. The calculation here is at zero temperature, and of course one should consider the wave vector **Q** of maximum susceptibility as a function of temperature. With this proviso, we find that the nesting vector determined from the maximum in the susceptibility from the energy band with open orbits is not that given by the usual point of inflection criterion, but rather by our criterion. For the family of compounds we consider here we have found that, as the nesting of the open Fermi surface deteriorates, the absolute maximum when both energy bands are taken into account can come from nesting vectors which give simultaneous touching of both the open and closed Fermi surfaces. To determine the absolute maximum of the total susceptibility its value must be calculated numerically at the small number of vectors for which either the open surfaces touch twice, or for which there is simultaneous touching of both the open and closed Fermi surfaces. These vectors are identified from the intersections of the lines of cusps constructed as in Fig. 4.

We should remark that in taking the criterion of the maximum noninteracting susceptibility for the instability in a multiband Hamiltonian, we are assuming that the interaction matrix is not only smoothly varying as a function of momentum but also has elements $U_{\alpha,\beta}$ that are independent of the band indices α and β. If we take a Hubbard-type interaction U that is diagonal on site, when it is transformed into the band representation, $U_{\alpha\beta}$ this condition is well satisfied over the Brillouin zone. It remains to be studied whether screening effects seriously modify this assumption.

We now turn to a few representative cases to illustrate these considerations. As mentioned before, within the mean-field theory in the limit of a short-range interaction the nesting vector that is ''best'' in the sense of maximizing the noninteracting susceptibility becomes the wave vector of the spin-density wave that is frozen in at low temperatures. The periodicity determined by the spin-density-wave potential should give rise to a reconstructed Fermi surface for the electrons. This Fermi surface can be qualitatively inferred if one displaces the original one by the **Q** vector as many times as necessary to recover a periodic picture. Degeneracies at the intersection of lines should then be removed by the effect of interaction, yielding the final reconstructed structure. Here we are faced with the first consequence of such a calculation: that the **Q** vectors obtained are incommensurable with the lattice; thus, in principle, a periodic picture is never recovered. However, if we consider the effect of the spin-density wave to first order or, alternatively, if the spin-density wave gives an undistorted helix, only intersections of surfaces related by a single displacement by **Q** are relevant. We show an example of this for the potassium compound in Fig. 5. There are a few interesting features in this figure that we would like to comment upon. First, there is no overlap of the closed pockets, although they are nearly touching. This disagrees with a picture such as that proposed by Kartsovnik, Kovalev, and Kushch,[14] where overlap of the closed pockets gives rise to small closed orbits and new open orbits with different orientation with respect to the high-temperature

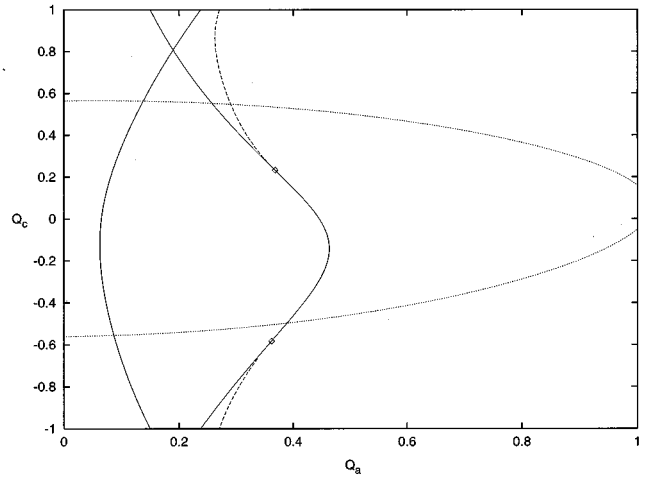

FIG. 6. The lines of cusps in the **Q**-dependent susceptibility of α-(BEDT-TTF)$_2$TlHg(SCN)$_4$.

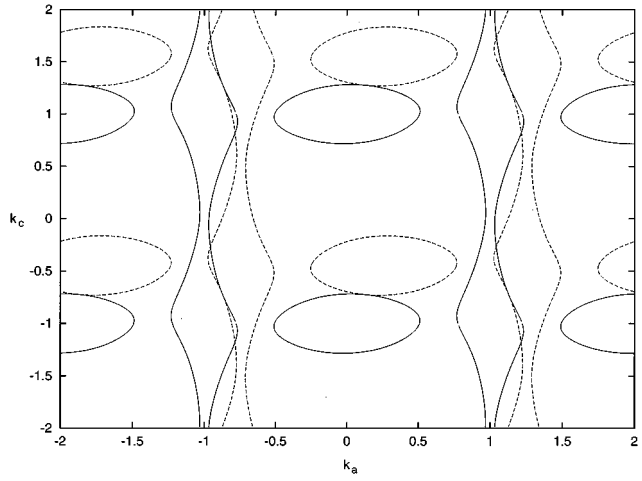

FIG. 7. Original and displaced Fermi surfaces of the thallium compound for the nesting vector that maximizes the *total* susceptibility. In this case the open branches are tangential at one point, and cross at another. The hole pockets also touch at one point.

ones. However, the area of the closed pockets obtained with the parameters that we are using is about 13% of the first Brillouin zone, rather smaller than that observed experimentally and assumed in Ref. 14. Thus, it is still possible to recover such a picture if the actual size of the pockets is larger, even if the **Q** vector that we calculated is not the same as proposed in Ref. 14. The second point of note in Fig. 5 is the presence of small closed orbits resulting from the imperfect nesting of the open branches of the Fermi surface. The area of the small closed regions shown in Fig. 5 is approximately 0.66% of the Brillouin zone. Considering that an orbit corresponding to 100% of the Brillouin zone would be experimentally observed as a frequency of about 4200 T, we would predict low-temperature oscillations of 28 T. Even assuming that the parameters are exact, this would actually be an upper limit, since the final pockets should have a smaller area due to the effect of the interaction that lifts the degeneracy at the points where the lines touch or cross.

As we have noted, the compound with potassium in the anion layer has a calculated band structure that is rather special in that a single nesting vector very nearly gives nesting at two points on the open Fermi surface and simultaneously on the hole pocket. If we look at other structures this is no longer true: the vector giving double nesting of the open surface does not give a touching of the closed hole pocket. In Fig. 6 we show the lines of cusps for the parameters calculated by Rousseau *et al.*[9] from the structure as measured for the compound in which thallium substitutes for potassium. Unlike the previous case, the two cusp lines related to nesting of the open Fermi surfaces intersect away from the lines of closed pocket nesting. From our numerical calculation the absolute maximum of the susceptibility for this case is at $\mathbf{Q}=(0.26\pi/a,\ 0.55\pi/c)$, where the pockets and open surfaces each touch once. A spin-density wave with this wave vector would give the translated Fermi surfaces shown in Fig. 7. Such a nesting would produce two low-frequency orbits from imperfect nesting of the open Fermi surfaces. The vector of double nesting for the open Fermi surface has a smaller susceptibility, and would give rise to a reconstruction as shown in Fig. 8. Such a state is, in principle, distinguishable from the previous low-temperature state, as there is a single frequency from imperfect nesting. For either of these vectors the hole pockets do not overlap with their translates. Thus, to lowest order in the spin-density-wave amplitude, there would not be additional low-frequency oscillations coming from the closed branch of the Fermi surface.

If we take the compound with ammonium replacing thallium, the calculated best nesting vector gives a reconstruction similar to that of Fig. 7. In addition, a competing vector with the open surface touching at two points gives a reconstructed Fermi surface that is rather different, as shown in Fig. 9. In this case the susceptibilities for the two wave vectors are very similar. Experimentally this compound has a low-temperature behavior very different from the previous two: rather than undergoing an antiferromagnetic transition it becomes superconducting. Surprisingly, the maximum magnetic susceptibility is higher than that for the potassium and thallium salts, which order antiferromagnetically at 8 and 9 K, respectively.

IV. CONCLUSIONS

We conclude that our nesting criterion, based on the coincidence of two quadratically nested points, can give a higher susceptibility than the single quartic nesting given by points of inflection. For the application developed here, i.e., determination of best nesting vectors for the spin-density-wave state of α-BEDT-TTF salts, it does indeed give the correct criterion for the susceptibility from the energy surface that contributes the open branches of the Fermi surface. As the open surfaces are poorly nested, there is competition from a simultaneous quadratic nesting of one point on the open Fermi surface and one on the closed. For these systems the contribution of the so-called ''two-dimensional'' band cannot be neglected in the calculation of the susceptibility. Knowledge of the geometry of the Fermi surface is enough to predict a small number of possible nesting vectors; numerical calculation is necessary to distinguish the most probable. The different forms of nesting give different numbers

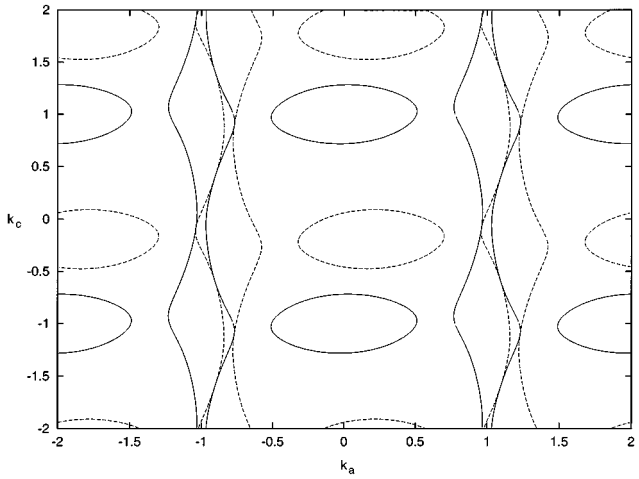

FIG. 8. Original (continuous lines) and displaced (dashed lines) Fermi surfaces of the thallium compound for the nesting vector that maximizes the *open* Fermi-surface contribution. The closed hole pockets do not overlap or touch.

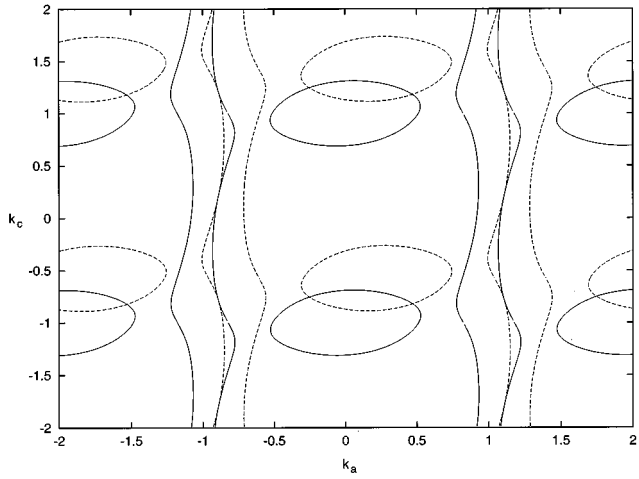

FIG. 9. Original and displaced Fermi surfaces of the ammonium compound for the nesting vector that maximizes the contribution of the *open* Fermi surface to the susceptibility. In contrast to Figs. 5, 7, and 8, the hole pockets overlap.

of low-frequency magnetic oscillations at low temperature due to small pockets caused by the imperfect nesting of the open and closed Fermi surfaces. Operationally it would be wisest to compare the experimental frequencies to each possible nesting.

In practice, both experimentally and theoretically, things are more complicated. Experimentally at low-temperature observation of three small frequencies for the thallium compound (10.8, 12.8, and 1.15 T) has been reported,[15] in addition to the basic frequency of 670 T that corresponds to the closed hole pockets of the high-temperature phase. Other experiments[14,16] give frequencies of 200, 670, and 870 T, consistent with a rather strong overlap of the closed pockets and no sign of the open ones. From a theoretical point of view we must include the possible overlap of the closed hole pockets and hybridization between the open and closed branches in the presence of the spin-density wave. Here we have also neglected the effect of spin splitting.

Since the experiments are carried out in finite magnetic field, a full analysis requires recalculation in the presence of such a field. This is more difficult than in the model of Gor'kov and Lebed',[12] since in that case exact propagators can be written even in finite magnetic field, due to the fact that the linearized spectrum eliminates the effect of the lattice in that direction. For the models considered here, with a tight-binding dispersion relation in both directions, it is not possible to solve the resulting quasi-periodic Hamiltonian. Given competing nesting vectors with different reconstructed orbits, it is likely that there are field-induced transitions between different spin-density-wave states, as occurs for TMTSF.[4]

Nonetheless, it is interesting that the small frequency that we would predict from the optimal nesting vector has a value much closer to experimental observations than that from the points of inflection where the pockets are a factor of 20 too large. In principle, our picture is more or less consistent with the observations of Uji *et al.*,[15] in that we predict low-frequency oscillations corresponding to small closed orbits that result from an imperfect nesting of the open Fermi surface. However, as we mentioned before, changes in parameter values may change, for instance, the areas of the hole pockets of the high-temperature Fermi surface, which could shift our results toward the picture proposed by Kartsovnik, Kovalev, and Kushch.[14] On the other hand, the high sensitivity of these compounds to pressure changes,[17,18,9] and thus probably to sample preparation, may explain the differences found between different experiments. The possible reconstructions we show in Figs. 5, 7, 8, and 9 demonstrate that only a very precise determination of the Fermi surface can give a firm prediction for a given compound.

We note that for both compounds that undergo a magnetic transition, if the calculated overlap parameters are taken to be correct, the correlation energy must be small to account for the low ordering temperatures, at least in the random-phase approximation (RPA). With critical temperatures near 10 K, a Hubbard-like U should be no more than a few tenths of an eV, rather smaller than values deduced from optical experiments in TTF salts[19] or κ-$(ET)_2Cu(NCS)_2$.[20] This may not be serious, as we know that a simple RPA seriously overestimates magnetic instabilities: we should renormalize the bare interaction by multiple scattering. For example, in the case of a single-band two-dimensional Hubbard model, Chen *et al.*[21] showed that good agreement between numerical results and a RPA treatment is obtained even for large values of the Hubbard interaction U, provided the bare Hubbard interaction is renormalized. Thus a weak-coupling approach as taken here may apply much longer than naïvely expected.

Even if there is still a large effective on-site U, as we would expect by comparison with other molecular conductors, the long-range order predicted by the RPA at relatively higher temperatures may be destroyed by thermal fluctuations enhanced by the quasi-two-dimensionality. To understand what is happening it would be useful to have direct measures of both the correlation energy and the interplanar coupling, since the stability of the long-range order depends on both. From our results, we have no immediate explanation why the NH_4 compound is not magnetic at low tempera-

tures, since the magnetic susceptibility is no smaller, and there are no obvious differences in the reconstructed Fermi surfaces. It is then possible that the main difference resides in changes of the interplanar coupling due to changes in the anion layer that separates two consecutive BEDT-TTF planes. The only clue we might deduce from the calculation in the plane is that the maximum of the susceptibility for the NH_4 compound is rather slowly varying along the cusp connecting the two competing nesting vectors. We might speculate that this can enhance quantum and thermal fluctuations sufficiently to suppress long-range magnetic order.

ACKNOWLEDGMENT

M.G. acknowledges support from the Brazilian agency Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

*Permanent address: Instituto de Física, Universidade Federal do Rio Grande do Sul, 91501-970 Porto Alegre, RS, Brazil. Electronic address: magusmao@if.ufrgs.br

†Current address: Institute Laue Langevin, B.P. 156, 38042 Grenoble Cédex, France. Electronic address: ziman@ill.fr

[1] T. Ishiguro and K. Yamaji, *Organic Superconductors* (Springer-Verlag, Berlin, 1990).

[2] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. **12**, 1125 (1973).

[3] K. Bechgaard, C. S. Jacobsen, K. Mortsen, J. H. Pederson, and N. Thorup, Solid State Commun. **33**, 1119 (1980).

[4] G. Montambaux, Phys. Rev. B **38**, 4788 (1988).

[5] G. Montambaux, Ph.D. thesis, Université Paris-Sud, Orsay, France.

[6] S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett. **50**, 270 (1983); E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. I. Bubarov, Pis'ma Zh. Éksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)]; H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. **1988**, 55.

[7] H. Mori, S. Tanaka, M. Oshima, G. Saito, T. Mori, Y. Murayama, and H. Inokuchi, Bull. Chem. Soc. Jpn. **57**, 627 (1984).

[8] L. Ducasse and A. Fritsch, Solid State Commun. **91**, 201 (1994).

[9] R. Rousseau, M.-L Doublet, E. Canadell, R. P. Shibaeva, S. S. Khasanov, L. P. Rozenberg, N. D. Kushch, and E. B. Yagubskii, J. Phys. (France) (to be published).

[10] L. P. Gor'kov and A. Lebed', J. Phys. Lett. **45**, L433 (1984).

[11] S. Jafarey, Phys. Rev. B **16**, 2584 (1977).

[12] J. S. Brooks, C. C. Agosta, S. J. Klepper, M. Tokumoto, N. Kinoshita, H. Anzai, S. Uji, H. Aoki, A. S. Perel, G. J. Athas, and D. A. Howe, Phys. Rev. Lett. **69**, 156 (1992).

[13] T. Osada, R. Yagi, A. Kawasumi, S. Kagoshima, N. Miura, M. Oshima, and G. Saito, Phys. Rev. B **41**, 5428 (1990).

[14] M. V. Kartsovnik, A. E. Kovalev, and N. D. Kushch, J. Phys. (France) **3**, 1187 (1993).

[15] S. Uji, H. Aoki, M. Tokumoto, T. Kinoshita, N. Kinoshita, Y. Tanaka, and H. Anzai, Phys. Rev. B **49**, 732 (1994).

[16] J. Caulfield, S. J. Blundell, M. S. L. du Croo de Jongh, P. T. J. Hendriks, J. Singleton, M. Doporto, F. L. Pratt, A. House, J. A. A. J. Perenboom, W. Hayes, M. Kurmoo, and P. Day, Phys. Rev. B **51**, 8325 (1995).

[17] P. Auban-Senzier, A. Audouard, V. N. Laukhin, R. Rousseau, E. Canadell, L. Brossard, D. Jérome, and N. D. Kushch, J. Phys. (France) **5**, 1301 (1995).

[18] C. E. Campos, P. S. Sandhu, J. Brooks, and T. Ziman, Phys. Rev. B **53**, 12 725 (1996).

[19] J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, Phys. Rev. B **19**, 730 (1977).

[20] F. L. Pratt, J. Singleton, M. Kurmoo, S. J. R. M. Spermon, W. Hayes, and P. Day, in *The Physics and Chemistry of Organic Superconductors*, edited by G. Saito and S. Kagoshima (Springer-Verlag, Berlin, 1990).

[21] L. Chen, C. Bourbonnais, T. Li, and A.-M. S. Tremblay, Phys. Rev. Lett. **66**, 369 (1991).