Symmetrized mean-field description of magnetic instabilities in
\(-\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2Y\) salts

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We present a novel and convenient mean-field method, and apply it to study the metallic/antiferromagnetic interface of \(-\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2Y\) organic superconductors \(\text{BEDT-TTF}\) is bis-ethylenedithio-tetrathiafulvalene, \(Y = \text{Cl, Br}\). The method, which fully exploits the crystal symmetry, allows one to obtain the mean-field solution of the two-dimensional Hubbard model for very large lattices (typically \(6 \times 10^5\) sites), yielding a reliable description of the phase boundary in a wide region of the parameter space. The metallic/antiferromagnetic transition appears to be second order, except for a narrow region of the parameter space, where the transition is very sharp and possibly first order. The coexistence of metallic and antiferromagnetic properties is only observed for the transient state in the case of smooth second-order transitions. The relevance of the present results to the complex experimental behavior of centrosymmetric \(-\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2Y\) salts is discussed.

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I. INTRODUCTION

The $\eta$-phase (BEDT-TTF)$_2$X salts exhibit a great variety of physical properties as a function of temperature, pressure, anion (X) substitution, deuteronation, and even disorder in the ethylene end-groups. Superconducting (SC), antiferromagnetic (AF), metallic and insulating phases are observed. Of particular interest is the AF/SC/metal boundary, which for (BEDT-TTF)$_2$Cu(NCS)$_2$ and (BEDT-TTF)$_2$Cu[N(CN)$_2$]Y (Y = Cl, Br; hereafter ET-Y family) occurs in a very narrow region of the temperature-pressure (T,p) space. For the aforementioned compounds, a schematic zero temperature phase diagram can be drawn as shown in Fig. 1. Universal zero temperature phase diagram for $\eta$-phase BEDT-TTF salts.

The proximity of SC and AF phases, together with other experimental evidence, suggested a possible role of spin fluctuations in the superconductivity mechanism and prompted intensive theoretical investigation on the SC/AF borderline. Since the early suggestion by Kino and Fukuyama, mean-field (mf) approaches have often been adopted to investigate the SC/AF interface. Several previous treatments considered low-symmetry structures, namely (BEDT-TTF)$_2$Cu(NCS)$_2$, with four inequivalent molecules in the unit cell. The resulting numerical calculation is complex and computationally very demanding, so that only fairly small lattices have been considered, leading to large intrinsic uncertainties on the estimated properties, particularly at the phase transition. On the other hand, in the orthorhombic centrosymmetric $\eta$-phase crystals of the ET-Y family, all molecules in the layer are equivalent. The greater symmetry with respect to (BEDT-TTF)$_2$Cu(NCS)$_2$, apparently does not lead to sign changes in the physical behavior, notably in the SC properties. Indeed, ET-Br is a superconductor at ambient pressure, and ET-C$_1$ under moderate pressure presents the highest $T_c$ observed in (BEDT-TTF)$_2$X salts. The mf approach has been applied also to these more symmetric lattices to study the coexistence of charge ordering and superconductivity. Including the order parameters relevant to charge instability further increases the complexity of the calculation and leads to large uncertainties in the transition region, as recognized by the authors of Ref. 3. We instead propose to fully exploit the higher symmetry of the centrosymmetric ET-Y and ET-C$_1$ structures to build a symmetric mean-field approach for the superconducting metallic/magnetically ordered phase transition. By exploiting symmetry we are able to work on lattices as large as $6 \times 10^5$ sites, and to explore a wide region of the parameter space, keeping numerical procedures and finite-size effects under control. Moreover, we most importantly, we get a simple and complete description of the electronic bands of these systems, focusing only on those eects which are directly connected with the interesting physics. The mf treatment maps the problem of interacting electrons into an effective non-interacting Hamiltonian. The comparison between reliable mf results and available experimental data then allows us to safely determine the intrinsic limitations of effective one-electron pictures in describing the physics of $\eta$-phase salts.

Recently more refined approaches have been applied to $\eta$-phase salts. For instance, correlation-exchange, FLEX, or third-order perturbation (PT) approaches have been applied to investigate the superconducting mechanism for superconductivity and to estimate the critical temperature. However, these approaches are only valid in the weak electronic correlation regime and have been applied to simple edge models for the $\eta$-phase layer, the so-called dimmer model. The same model has also been adopted in the framework of the dynamical mean-field theory, and in a renormalization group approach, which offers complementary information with respect to ordinary mean-field techniques. As we shall discuss in the following, the reliability of the dimmer model cannot be taken for granted in the whole parameter space. Here we show that by exploiting the high symmetry of the ET-Y family, one can get a picture of the $\eta$-phase layer that is computationally and theoretically as simple as the dimmer model, without introducing any approximation.

In this paper we omit the system in terms of a simple Hubbard, $t$-U, Hamiltonian, but the proposed procedure can be easily extended to $t$-U-V-J Hamiltonians to investigate charge-ordering transitions, whose possible coexistence with spin-order has been recently suggested. Moreover, the symmetry properties can be conveniently implemented in more refined calculation schemes to get simpler and more reliable description of the physics of $\eta$-phase salts. The paper is organized as follows. The next section is devoted to the description of the method. We then analyze the magnetic instabilities of ET-Y salts, and discuss the eects of the instabilities on the band structure. The di erence between our symmetrical mmf and the other mf approaches is stressed, and the reliability of the dimmer model is shortly addressed. Finally, we make connection with the experimental by discussing the pressure dependence of the SC/AF interface in the ET-C$_1$, and by making a comparison with ambient pressure ET-Br superconductor.
II. THE SYMMETRIZED MEAN FIELD APPROACH

Consistently with experimental data on centrosymmetric phase salts, we consider a unit cell with 4 equivalent molecular sites, and do not allow for modification of the periodicity of the crystal structure at the magnetic phase transition. We adopt the two-particle Hubbard Hamiltonian to describe Coulomb interactions giving rise to magnetic ordering:

\[ H = \sum_{ij} t_{ij} (n_i^+ a_j + h.c.) + \frac{U}{4} \sum_{i} n_i n_i' s_i s_i' \]

where the indices run on the BEDT-TTF sites, the first term accounts for the on-site Coulomb repulsion, and the other terms describe the on-site Coulomb repulsion. In eq. (1), \( n_i \) is the usual site number operator \( n_i = n_{i^+} + n_{i^-} \), and \( s_i = n_{i^+} - n_{i^-} = 2 \) is the net magnetization operator.

In the mf approximation the many-body interaction is described by an effective single particle interaction, where each particle feels the other particles as a source of a mf potential. Then each product of two electronic operators \( A^B \) is approximated with an expression where only a single operator appears, the effect of the second operator being substituted by its ground-state expectation value. This approach gives reliable results when the uncertainties of the observables are small, although not zero as in single-particle approaches. Mathematically:

\[ A^B = (n_i a_i^+ + n_i^+) (n_i b_i + n_i^+) \]

Thus in mf the two-particle Hubbard terms of eq. (1) become:

\[ \frac{U}{4} \sum_{i} n_i n_i' s_i s_i' \]

The equivalence of the four molecular sites imposes the constraint:

\[ n_i^+ + n_i^- = 1 \Rightarrow i = 1 \ldots 4 \]  

Therefore the first term on the r.h.s. of eq. (1) is a constant, and the relevant physics is described by the net magnetization term. We rewrite it by exploiting symmetries, and denote within each unit cell the following four order paramaters:

\[ \begin{align*}
A_F^1 &= (s_1^+ + s_2^+ + s_3^+ + s_4^+) \\
A_F^2 &= (s_1^- + s_2^- + s_3^- + s_4^-) \\
A_F^3 &= (s_1^- + s_2^- + s_3^- + s_4^-) \\
F_M &= (s_1^+ + s_2^- + s_3^- + s_4^+) 
\end{align*} \]

or, in short: \[ P_i c_i s_i, \text{ with } P = A_F^1, A_F^2, A_F^3, F_M \]. In these equations \( i \) counts the four BEDT-TTF sites within the unit cell, as indicated in Fig. 2. The order parameters \( A_F^1, A_F^2, A_F^3 \) correspond to the three possible antiferromagnetic orderings; \( \tilde{F}_M \) describes the ferromagnetic phase. The net magnetization term in Eq. (3) then becomes:\[ \sum_{ij} t_{ij} (a_i^+ a_j + h.c.) X_j Y_i \]

where \( t_{ij} \) are the hopping parameters, \( a_i \) and \( a_j \), and \( X_j \) and \( Y_i \) are defined in Fig. 2. For each symmetry, the effective single particle potential \( Y \), is related to the expectation value of the relevant order parameter by the self-consistency equation:

\[ Y = \frac{U}{2} \sum_{i} h_i \]

FIG. 2. Schematic view of the ac plane of centrosymmetric BEDT-TTF salts.

By rewriting the last term in eq. (5) in terms of the original \( n_i, a_i^+ \) operators, one immediately recognizes that \( H \) is the sum of two independent tight-binding Hamiltonians, \( -H \), describing electrons with up and down spin, respectively. The off-diagonal part of each one of these Hamiltonians is exactly the same as in the original tight-binding model, but the mf treatment of on-site electron-electron interaction introduces a diagonal contribution. Specifically, the diagonal elements of \( H \) within each unit cell are:
and $(H^{-})_{ij} = (H_{ij})_{ii}$. The two tight-binding problems described by $H^{-}$ and $H_{ij}$ are easily diagonalized for different $Y$ values on very large lattices. In our approach imposing the self-consistency relation on $U$ simply implies the rationing of $\Upsilon$ and $h_{ij}$, at variance with the lengthy and memory consuming iteration steps required by a multi-parametric method calculation. This is very important in keeping the numerical procedure under control and allows us to work with very large lattices, typically up to 6,000 sites. Such large lattices, one order of magnitude larger than the largest lattice in Ref. [3], are diagonalized with no effort on a Digital Alpha 255 workstation equipped with 64 M B RAM. As we will discuss below, working on large lattices is very important to get an accurate description of the early stages of the phase transition, and then to get reliable information on the nature of the transition itself.

The diagonalization of $H$, $H_{ij}$ immediately defines the band structures for up and down spins. In the case of the FM instability, all the $\delta_{Y}$ in eq. (8) are equal to 1, so that, apart from a rigid shift of the energies by

\[ Y_{FM} = \sum_{i} Y_{i} = 4 \text{ for up (down) spins, the eigenstates are exactly the same as in the non-interacting case. Therefore, the originally degenerate bands for up and down spins are split by } Y_{FM} = U_{FM} \text{.}

The Fermi level is fixed by the conservation of the total number of electrons, leading to unbalanced up and down spin population. Without loss of generality, we consider positive $h_{FM}$, we end up with lower energies for up spins and then with a ferromagnetic state characterized by larger population of up than down spins.

In the case of AF order, instead, nine $Y$ define the original bands of the non-interacting system, due to the appearance of relevant diagonal terms in the real space Hamiltonian (eq. [3]). In this case, the eigenvalues for up and down spins are the same $e$, and the bands for the two spins stay exactly degenerate as in the non-interacting case, but the distribution of the two spin species is different on the sites, with a larger number of up spins residing on sites with negative $c_{i}$ coe cients ($h_{AF} > 0$).

III. RESULTS

Table 1 summarizes the t's obtained from the available structural data of ET-Cl and ET-Br salts. All t's have been obtained from extended Huckel (EH) calculations on the pairs of BEDT-TTF molecules corresponding to the four interactions depicted in $g_{ij}$. Specifically, they are evaluated as half of the splitting of the HOMO energy in each pair. It is well known that the values of the hopping integrals show large di erences depending on the method adopted for their estimations. Therefore, the t's estimated for each structure and the resulting $U$ have not to be assigned too much confidence. However, comparing results obtained with the same procedure on di erent structures is certainly informative. We have adopted EH estimations of $t$'s since they compare well with available ab initio results.

![FIG. 3. ET-Cl at T = 127 K, ambient p: t's from the 1st row of Table 1. The order parameter for FM instability (squares) and AF instability of type 1 (circles) vs the active m potential, in the left panel, and vs U in the right panel. Filled circles mark points introduced in the linear regression of the vs. Y to determine $U_{o}$ (see text), the arrow marks the point where the conduction gap opens, and whose band structure is shown in g.](image)

The figure reports the Y and U dependence of $h_{AF1}$ and $h_{FM}$ order parameters, as obtained for the t's relevant to ET-Cl at 127 K (1st row in Table 1). $h_{AF1}$ and $h_{AFi}$ curves are not shown since the corresponding instabilities occur at $U$ larger than 1 eV and are not relevant to our discussion. Indeed, even the ferromagnetic instability occurs at $U$ higher than that for AF instabilities, and, in this respect, it is irrelevant from the physical point of view. However, the di erent behavior of $h_{AF1}$ and $h_{FM}$ in the right panel of g. then corresponds to unstable states, i.e. states that cannot be reached by our physical system. Thus the ferromagnetic instability corresponds to a 1st order phase transition, characterized by a discontinuous jump of the order parameter at the transition, located at $U_{c} = 0.945$ eV. The small region around $U_{c}$, where the $h_{FM}$ (U) non-single-valued corresponds to the hysteresis region, where two stable states coexist.

The behavior of $h_{AF1}$ is di erent, with $h_{AF1}(U)$ having in nite slope at $U_{c} = 0.64$ eV. This is a direct consequence of a strictly linear $h_{AF1}(U_{AF1})$ dependence in a fairly large region around the origin. In g. 3 left panel, the red circles show the points that fall on a single straight line, $h_{AF1} = Y_{AF1}$, with a squared correlation coe cient larger than 0.99998.
By applying the self-consistency condition in eq. (1), one immediately gets steeply increasing $A_{\text{FI}}$ values at a fixed $U = U_c = 2\pi = 0.639$ eV. The coefficient $= \theta^2 E = \theta^2 Y_{\text{AFI}}$ represents the susceptibility of electronic system to the $Y_{\text{AFI}}$ perturbation; the critical $U$ is thus related to the inverse of the electronic susceptibility.

Extracting $U_c$ from the slope of the $h_{\text{AFI}}$ vs $Y_{\text{AFI}}$ curve is a much safer procedure than searching for the minimum $U$ where $h_{\text{AFI}}$ appears. The calculated $h_{\text{AFI}}$ values are affected by renormalization, with a minimum intrinsic uncertainty given by the inverse of the number of unit cells. Since $h_{\text{AFI}}$ enters the Hamiltonian matrix as a multiplicative factor for $U$, the uncertainty in $h_{\text{AFI}}$ implies an uncertainty in $U$, with $U = 0 = h_{\text{AFI}} = h_{\text{AFI}}$. Therefore, at small $h_{\text{AFI}}$ the relative uncertainty on $U$ is very large. This is by no means accidental, but results from the limitations of investigating phase transitions through finite size calculations. At the transition in fact the correlation length of the fluctuations in the order parameter is in principle finite, so that calculations on finite lattices lead to large errors.

It is interesting to investigate the evolution of the electronic bands along the AF transition. Fig. 4 reports the band structure calculated for the non-interacting metallic system, and for a system located just where the transition goes to completion, i.e., the point marked by an arrow on $g_{\text{FI}}$. The two conduction bands, that are partly overlapped in the metallic system, are split apart in the AF phase, opening a gap and then leading to insulating behavior. Fig. 5 reports the $U$-dependence of the energy difference between two extremal points in the two conduction bands (specifically between $M$-point in the upper band and $X$-point in the lowest conduction band) to measure the conductivity gap. Negative implies overlapping bands and then metallic behavior, positive measures the semiconducting gap.

In summary, for the t's in the first row of Table I, relevant to ET-Cl at ambient pressure and $T = 127$ K, we observe a fairly sharp transition, at $U_c = 0.639$ eV, from a paramagnetic metal to an antiferromagnetic insulator, as shown by the semiconducting gap that opens up right at the transition (g. 3). In our approach the metallic phase includes the superconducting state, since our Hamiltonian does not account for SC coupling. The critical $U$ is similar to available experimental and theoretical estimates of the effective $U$ in BEDT-TTF salts, $U = 0.5 - 1.0$ eV. Therefore ET-Cl is just located at the metallic/AF interface, in agreement with several experimental observations (see below). A gain, in agreement with experiment and also with predictions of previous self-consistent calculations, the AF phase is characterized by parallel quasi-one-dimensional bands (g. 3), as could also be inferred from simple arguments based on the dimer picture.

Having developed a simple and elegant method to solve the MFT problem for the ET-Y family, we can now play around with parameters trying to gain some information about the rich phase diagram of these systems. In g. 5 the continuous lines show the $U$-dependence of $h_{\text{AFI}}$ and its calculated for the available t's relevant to ET-Cl at $p = 3$ and 27 kbar (Table I). The critical $U$ increases with $p$ from $0.64$ eV at $T = 127$ K, and ambient $p$, to $0.68$ eV and $0.91$ eV, at ambient $T$ and $p = 3, 27$ kbar, respectively. The increase of $U_c$ corresponds to a stabilization of the metallic phase, and can justify the appearance of SC in ET-Cl under pressure, as we shall discuss in more detail in next Section.
ever, the width of this region is only 2-3 times the numerical uncertainty on $U$, so that we cannot make any strong statement about observing a discontinuous, 1st order transition. In any case, the coexistence region, i.e. the hysteresis region for this transition, if present, would be so small as to be irrelevant for any practical purpose. The region of negative slope disappears at $p = 27$ kbar, where the transition looks smooth, with possibly a near positive slope. None of the effects is tiny and hardly disentangled from numerical uncertainties.

Similar to that discussed at length in Ref. [2]. However, the extent of this phase is very narrow, so that it represents at most a transient phase.

Searching for some evidence of discontinuous phase transition, we have also "released the pressure", by extrapolating the $t'$ estim ates at $p = 3$ and 27 kbar down to a nominal pressure of 33 kbar. Surprisingly, the transition is continuous again, at same other than at ambient $p$. Therefore, we find no clear evidence for discontinuous transitions, except possibly in a very narrow region in the parameter space corresponding to ET-Cl at $p = 3$ kbar. In general, the observation of very narrow regions of discontinuity and/or AF-metallic coexistence is strongly affected by numerical uncertainties and/or finite-size effects. These transient states, being intrinsically unstable, cannot be associated with physically significant states. On the other hand, their presence for particular values of the parameters signals an intrinsic instability of the system to environmental perturbations, such as those eventually leading to superconductivity.

**IV. DISCUSSION**

Overall, our results agree with previous calculations on -(BEDT-TTF)$_2$Cu(NCS)$_2$[3], describing the transition from a paramagnetic metal to an AF insulator occurring at $U_c = 0.6-0.8$ eV (the precise value of course depends on the choice of the $t'$). However, some details on the evolution of the order parameter and on the opening of the semiconducting gap are different. In the recursive approach to the solution of the mfp problem, adopted so far in the literature, the only viable procedure to estimate $U_c$ relies on searching for the m inimum $U$ where the $h_{AF}$ appears. As discussed above, this procedure leads to large uncertainties in $U_c$, that have to be properly accounted for in the analysis of numerical results. Kino and Fukuyama also use very small lattices ($N = 3600$), corresponding to an intrinsic uncertainty in $h_{AF}$ of at least $4 \times 10^{-4}$. In Ref. [3], they estimate $U_c$ to be $0.762$ eV, which is $0.02$ eV lower than the onset of AF insularity in $U_{cl} = 0.02$ eV. The two transition points observed by Kino and Fukuyama at $U_{cl} = 0.762$ eV and $U_{cl} = 0.758$ eV, coincides with numerical accuracy. In the lack of additional information their data are consistent with a single transition, whereas our data for the $t'$ relevant to ET-Cl at $T = 127$ K or at $p = 3$ kbar (Ref. [4]). The presence of an antiferromagnetic metallic phase is then questionable. Similar problems occur in the interpretation of data in Ref. [5]. Here a two-transition scenario is proposed at low $p$, involving a continuous transition from a paramagnetic metal to an antiferromagnetic metal (- AF and negative), immediately followed by a 1st order transition to an insulating state. This complex scenario, that we were unable to reproduce in our large lattice for any choice of the parameter set, is prob-
by either a finite-size effect or a numerical artifact. One must also keep in mind the possibility it represents a characteristic feature of \((BEDT-TTF)_2\text{Cu(NCS)}_2\), due to its lower symmetry. However, since it does not appear in the more symmetric ET-1Cl phase at any pressure, it is irrelevant as far as SC is concerned.

In Ref. 2, the numerical uncertainty in \(h_{AF1}\), noted by the authors at 0.001, propagates to give \(h_{AF1} \approx 0.0014\). As a consequence, the estimate for \(U_3\), i.e. the critical \(U\) for the appearance of AF order, obtained for \(h_{AF1} = 0.01\), is aected by a large uncertainty: \(U_3 = 0.7 \pm 0.01\). More precise estimates are obtained for larger \(h_{AF1}\), e.g. \(U_3 = 0.685\) is essentially constant for \(h_{AF1} = 0.037, 0.499, 0.582\), representing a good estimate for the critical \(U\) where AF order appears and, at the same time, the electronic orbits close. The proposed estimate for the critical \(U\) for the opening of the semi-conducting gap, \(U_1 \approx 0.699\), is different from \(U_3\), again suggesting the presence of an intermediate phase with both metallic and AF character. Quite in agreement with our results at large \(r\), the metallic antiferromagnetic phase is a marginal phase that only survives in a very narrow transient regime. Indeed, as pointed out in Ref. 30 (Section 3.4.5), such a phase would imply a weak AF order and reconstruction of the Fermi surface, which however have not been experimentally observed.

Our approach thus proves useful in excluding on a purely theoretical basis the spurious complexities in the phase diagram due to finite-size effects and/or numerical uncertainties, and should be particularly convenient when extended to describe charge ordering instabilities together with magnetic instabilities.

Several papers discuss phase BEDT-TTF salts within the the dimer approximation [32,33]. Basically, the tight-binding Hamiltonian for the four frontier molecular orbitals in the unit cell is rewritten in terms of the bonding and antibonding orbitals of the \(t_{b1}\)-dimers. Since \(t_{b1}\) is at least twice as large as the hopping integrals, the interactions between bonding and antibonding orbitals are neglected, and the original four-bands problem reduces to a two-band problem. In the resulting lattice each site has four nearest-neighbor sites, interacting through \((t_0 + t_1) = 2\), and two next nearest-neighbors, interacting with \(t_5 = 2\). For the paramters relevant to \(K\)-phase salts, the bands calculated within the dimer model compare favorably with those obtained in the four-band calculation, confirming the validity of the dimer model approximation at least for the non-interacting case.

The dimer model lattice is simple, but still shows interesting physics. In fact, by varying the \((t_0 + t_1)/t_5\) ratio, it interpolates between a square lattice and a collection of 1D chains [32,33]. However, it is suggestive to relate the variegated behavior obtained from such a model to the variety of observed properties for phase salts, some caution is in order. Just as an example, consider the case \(t_5 = 0\), where the dimer lattice reduces to a half-filled square lattice with perfect nesting. As it is well-known, the critical \(U\) for the antiferromagnetic instability goes to zero in this limit, as also confirmed by mfcalculations [31,32].

Instead, a mfc calculation for the same parameters as in g. 3, but \(t_0 = 0\), yields a continuous transition to the AF phase with a finite and fairly large \(U_{AF} \approx 0.57\). This qualitative difference in behavior can be easily rationalized: The small interactions between bonding and antibonding orbitals are large enough to break the commensurability of the simple dimer model at \(t_0 = 0\). A word of caution is also necessary when introducing electron correlations in the dimer model. Indeed, starting from a Hubbard Hamiltonian for the four-molecules layer, the resulting effective \(U_{dim}\) for the dimer model is related to both \(U_3\) and \(t_{b1}\), according to a relation not proposed in Ref. 2, and discussed and extended in Ref. 3. For the commonly accepted value of \(t_{b1} = 0\), \(U_{dim}\) is of the order of \(t_5\) [34,35]. Thus the applicability of mfc and perturbative approaches [34,35] to the dimer model becomes questionable, since these approaches work well in the \(\pm U_{dim} \approx 1\) regime and/or extremely large pressures, have been shown. The fully deuterated ET-1Cl (4\text{h}-ET-Cl) exhibits analogous behavior, only requiring a slightly higher pressure (440 bar) to reach superconductivity [36,37]. ET-Brs is superconducting at ambient pressure \(T_c \approx 11\) K but the attainment of the superconducting phase is aected both by the cooling rate and by the deuteration of the same salts. This has been shown that by keeping constant the cooling rate at a sufficiently low value, the partially deuterated \(d_2\)- and \(d_3\)-ET-Brs salts are superconducting at practically the same \(T_c\) as the undeuterated sam ple. The \(d_2\)-salt, on the other hand, exhibits a complicated behavior attributed to the competition between superconducting and insulating phases. Finally, the fully deuterated \(d_3\)-ET-Brs is an antiferromagnetic insulator in magnetic com ent; \(0.3\) and under pressure has a behavior similar to ET-1Cl, reaching complete superconductivity just above 60 bars. For the sake of completeness, we mention that the ET-I salt is not superconducting, even when pressures up to 5 Kbars are applied. This kind of behavior has been ascribed to disorder. However, this compound is the least investigated in the ET-Y family, and we shall not consider it here.

Rather obviously, a mfc approach is inadequate to describe phenomena related to non-equilibrium states, disorder and/or sample inhomogeneity, like cooling rate effects and reentrant superconductivity. We therefore focus...
here on the complete-SC/AF crossover acted by pressure and/or isotopic substitution. The universal phase diagram in $g_{\alpha\beta}$ presents the parameter $p$ pressure as the abscissa. It has been used to explain the differences induced by the Cl-Br substitution or deuteration in ET-Y salts, and similar eects. In particular, the smaller radius of Cl with respect to Br implies a reduced eective pressure in ET-Cl with respect to ET-Br (see Ref. 3 for a tentative numerical assessment of this eect). A similar eect of reduced pressure can be associated to deuteration, which corresponds to smaller end-group excursions around their equilibrium values. From the values of the corresponding $T_c$'s, we can empirically associate an increase in $p$ of 380 bar for the Cl-Br substitution, and a decrease of 140 bar for deuteration. A rationalization of these tiny eects is fairly diicult. We shall examine below whether our results help in this respect.

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The pressure dependence of the ratio between the areas of and orbits in the ac plane Fermi surface. The squares refer to the experimental data (Ref. 2), with the dashed line representing the best linear fit. Circles are the calculated values.

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We first focus on ET-Cl. The hopping integrals in the ac plane, calculated for the known crystal structures at ambient $p$ and 127 K $p_0$ and at 3 and 28 kbar (ambient $T = 24 K$) are reported in Table 1. To make a rough comparison with experiment, we have evaluated the areas of the and orbits from the ac plane Fermi surface calculated in the tight binding approximation. The results relevant to the metallic phase are compared in $g_{\alpha\beta}$ with the measured areas from Shubnikov-de Haas (SDH) experiments performed at several pressures in the 2-10 kbar range at the liquid Helium temperature. In order to interpret the observed $T_c$ values, the ratio has been reported as a function of pressure. In fact, the area is equal to the area of the Brillouin zone for the 3/4-liked system. The 3 kbar = $T_c$ in the experiment, and a straight line through the experiment points extrapolates near to the calculated 28 kbar point. However, we notice that the crystallographic axes ratio $c_a$ is practically unchanged with pressure. This observation sheds doubts on the possibility of adopting $c_a$ as a rough estimate of $c_b$, as suggested by Ref. 2.

Figure 7, rightmost column, reports the ET-Cl $U_c$ values calculated by our approach. A word of warning is necessary when comparing data obtained at different temperatures, since it has been observed $U_c$ that the values of the hopping parameters change correspondingly. However, this eect is not very pronounced in ET-Y and ET-Br (SC) and we shall neglect $U_c$ in the following. We notice that $U_c$ increases monotonically with $p$, thus accounting for the pressure driven superconductivity transition in terms of an increase of the critical value needed to reach the AF phase. In this respect, $U_c$ seems to be a good indicator of the eective pressure of $g_{\alpha\beta}$. Other previously suggested indicators, like the $t_{ub}/t_{pu}$ ratio, do not seem to work less satisfactorily in this case: $t_{ub}/t_{pu}$ does not increase monotonically with $p$ (Table 2), and, as noted above, $c_a$ is practically constant.

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We now turn to ET-Br. When comparing the ambient pressure, 127 K hopping integrals of ET-Cl with the corresponding ones of ET-Br, one finds small differences, and we get for the two systems virtually identical phase transitions, occurring at basically the same $U_c$ (Table 1). Therefore, the diereent ground state of ET-Cl (AF) and ET-Br (SC) at ambient pressure cannot be understood in terms of a diereent $U_c$. One might think that the actual eective $U_c$ is diereent in the two types of salts, being smaller in ET-Br due to a larger screening of the internode Coulomb potential from the more polarizable Br anions. However, this kind of qualitative explanation is not corroborated by the numerical values of the $g_{\alpha\beta}$ obtained from ab initio calculations, and it is diicult to reconcile with the observation of an AF state for $d_{12}$-ET-Br at an ambient pressure. We could not calculate the hopping integrals in this case, as the atomic coordinates are not available in the literature. We have used the calculated in Ref. 2 for both ET-Br and $d_{12}$-ET-Br at 127 K (properly rescaled since the method of calculation is different from ours). We do not nd significant diereence between the $U_c$'s of the two compounds.

As we already pointed out, $c_a$ or $t_{ub}/t_{pu}$ are not good indicators of the properties of phase salts, and cannot be chosen as the $x$-axis parameter in a universal phase diagram like that reported in $g_{\alpha\beta}$. Both the ratio of and orbits and $U_c$ work satisfactorily as far as the $p$-dependence of ET-Cl properties is concerned. However, both fail if applied to rationalize the diereent behavior of ET-Cl and ET-Br and/or the eects due to deuteration. It is important to underline that both and $U_c$ are "single particle" parameters, in the sense that they isolate the band structure, i.e., the $t_c$'s values. Investigating the band structure of -phase
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| System      | $t_{11}$ | $t_{12}$ | $t_p$  | $t_q$  | $U_c$  |
|-------------|----------|----------|--------|--------|--------|
| ET-CI, amb. p, T = 127 K | 0.2315   | 0.0760   | 0.0901 | 0.0410 | 0.639  |
| ET-CI, p = 3 Kbar, am b. T | 0.2239   | 0.0851   | 0.0844 | 0.0517 | 0.676  |
| ET-CI, p = 27Kbar, am b. T | 0.2770   | 0.0935   | 0.1400 | 0.0380 | 0.906  |
| ET-Br, amb. p, T = 127 K | 0.2244   | 0.0712   | 0.0936 | 0.0396 | 0.636  |

TABLE I. Hopping integrals and critical $U$ for ET-C1 and ET-Br salts. All parameters in eV.