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2006 J. Phys.: Condens. Matter 18 L575

(http://iopscience.iop.org/0953-8984/18/46/L01)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) L575–L584 doi:10.1088/0953-8984/18/46/L01

**LETTER TO THE EDITOR**

# Mixed order parameters, accidental nodes and broken time reversal symmetry in organic superconductors: a group theoretical analysis

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Received 10 August 2006, in final form 14 September 2006
Published 3 November 2006
Online at stacks.iop.org/JPhysCM/18/L575

**Abstract**

We present a group theoretical analysis of several classes of organic superconductor. We predict that highly frustrated organic superconductors, such as $\kappa$-$(ET)_2Cu_2(CN)_3$ (where ET is BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene) and $\beta'$-$[Pd(dmit)_2]_2X$, undergo two superconducting phase transitions, the first from the normal state to a d-wave superconductor and the second to a $d + id$ state. We show that the monoclinic distortion of $\kappa$-$(ET)_2Cu(NCS)_2$ means that the symmetry of its superconducting order parameter is different from that of orthorhombic $\kappa$-$(ET)_2Cu[N(CN)_2]Br$. We propose that $\beta''$ and $\theta$ phase organic superconductors have $d_{xy} + s$ order parameters.

(Some figures in this article are in colour only in the electronic version)

One of the most basic questions that can be asked about any phase of matter is, what symmetries does it spontaneously break? For example, all superconductors break gauge symmetry but many also break additional symmetries [1–3]. Organic charge transfer salts are an important class of superconductor because they are highly tunable and have a number of exotic properties [4–7] such as a small superfluid stiffness [8, 9], a Mott transition with an exotic critical point [10], spin liquid states [11, 12, 14], a 'bad metal' [13], pseudogap-like behaviours [15], and charge ordered states [16]. Many of these properties are analogous to those of the cuprates [17] and cobaltates [18]: this has heightened interest in organic superconductors as model systems. Yet, in spite of two decades of intense effort, many basic questions remain unanswered. Of particular importance is the, still controversial, question of what is the symmetry of the superconducting state [19, 20].

In this work we use group theory to analyse the symmetries of the superconducting states in these materials. We discuss the pairing symmetries of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$ which we argue are '$d_{x^2-y^2}$'. We show that for $\kappa$-$(ET)_2Cu(NCS)_2$ to

  

have a similar superconducting state requires the existence of accidental nodes (i.e., nodes that are *not* required by symmetry). Thus although the state may be correctly described as 'd-wave', neither a '$d_{x^2-y^2}$' nor a '$d_{xy}$' is to be expected. Extending these arguments allows us to predict that highly frustrated materials such as $\kappa$-$(ET)_2Cu_2(CN)_3$ and $\beta'$-$[Pd(dmit)_2]_2X$ will[1] undergo two superconducting transitions, the first from a normal metal to a 'd-wave' superconductor and the second from a 'd-wave' superconductor to a '$d + id$' state which breaks time reversal symmetry. Similar reasoning implies that $\theta$-$(ET)_2I_3$ and $\beta''$-$(ET)_2SF_5CH_2CF_2SO_3$ have '$d_{xy} + s$' order parameters.

Group theory provides a powerful tool for addressing the symmetries of superconducting states as it does not assume any particular microscopic mechanism or theory of superconductivity [1–3]. Such approaches are vital for the organic superconductors where there are clear signs that BCS theory, and indeed weak coupling approaches in general, are not sufficient to explain the observed experimental results, particularly the small superfluid stiffness [8, 9]. The small superfluid stiffness observed in materials far from the Mott transition is qualitatively different from the predictions of BCS theory (which predicts that the superfluid stiffness is smallest near the Mott transition [9]). More generally any weak coupling theory will suffer from this problem and fail to predict either the large effective masses observed experimentally [5] or the existence of the Mott transition [10]. The properties of nodal quasiparticles, which are determined by the symmetry of the superconducting state, have proved crucial in both the superconducting and pseudogap states of the cuprates [21].

Labels like '$d_{x^2-y^2}$' are taken from the expansion of the order parameter in terms of spherical harmonics, appropriate to the superfluid. However, for a superconductor the correct label for a superconducting state is the irreducible representation of the point group of the crystal which the order parameter transforms like under the operations of the point group [1–3, 6]. Thus one should say that tetragonal cuprate superconductors have $B_{1g}$ symmetry but this is often described as a '$d_{x^2-y^2}$' state. The description of superconducting states by analogy with spherical harmonics is widespread, but must be used with care as, for example, not all crystals support '$d_{x^2-y^2}$' states. In particular we will see that this is not a possibility is the monoclinic organic superconductors discussed below.

Organic superconductors form several allotropes. The observed behaviour of the $\beta$, $\beta'$, $\kappa$, and $\lambda$ phases is very different from that of the $\beta''$ and $\theta$ phases. These differences arise because in the former phases the ET molecules are strongly dimerized. That is the hopping integral between pairs of the ET monomers is larger than the other intermolecular hopping integrals (see figure 2). In the $\beta''$ and $\theta$ phases the dimerization is weak or absent [16, 22, 23]. We begin by studying the strongly dimerized materials. From a group theoretical perspective we may separate these into three broad classes: those with orthorhombic unit cells (e.g., $\kappa$-$(ET)_2Cu[N(CN)_2]Br$); those with monoclinic unit cells (e.g., $\kappa$-$(ET)_2Cu(NCS)_2$); and those with highly frustrated band structures (e.g., $\kappa$-$(ET)_2Cu_2(CN)_3$).

Experimentally, the pairing symmetries of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$, $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$, and $\kappa$-$(ET)_2Cu(NCS)_2$ are not fully determined. However, all show signs of unconventional superconductivity: there are no Hebel–Schlicter peaks [15], the thermodynamic measurements performed to the lowest temperatures show a power law temperature dependence[2], the disorder strongly suppresses the superconducting critical temperature [20, 25] and a zero-bias-conductance peak has recently been observed in $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ [26]. Collectively

[1] $X = Me_4Z$, $Et_2Me_2Z$; $Z = P$, Sb; $Me = CH_3$ and $Et = C_2H_5$.

[2] Carrington *et al* [24] measured the penetration depth of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu(NCS)_2$ down to 0.4 K and observed power law dependences, although other measurements (which did not go to such low temperatures) have found exponentially activated behaviours occur in the same materials, e.g., Elsinger *et al* and Müller *et al* [24]. For a more detailed discussion see [20].

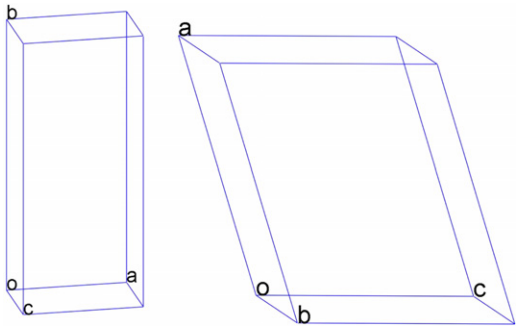


**Figure 1.** The symmetry of the unit cells of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ (left) and $\kappa$-$(ET)_2Cu(NCS)_2$ (right). $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ has an orthodromic unit cell which is symmetric under the identity, reflection by $\pi$ about the $a$, $b$ and $c$ axes (the $z$ axis and the two diagonals of the $xy$ plane), reflection through the $ab$, $ac$ and $bc$ ($z\{x+y\}$, $z\{x-y\}$ and $xy$) planes and inversion. Therefore the symmetry of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ is represented by the group $D_{2h}$. $\kappa$-$(ET)_2Cu(NCS)_2$ has a monoclinic unit cell which is symmetric under the identity, rotation by $\pi$ about the $c$ ($x$–$y$) axis, reflection through the $ab$ ($z\{x+y\}$) plane and inversion. This symmetry is represented by the $C_{2h}$ point group.

**Table 1.** The symmetry required nodes and some basis functions of the even parity irreducible representations (irrep) of the point group $D_{2h}$. This is the symmetry of the orthorhombic organic superconductors such as $\kappa$-$(ET)_2Cu[N(CN)_2]Br$, in which the highly conducting plane is the $a$–$c$ plane, i.e., $k_z \parallel b$, and $\theta$-$(ET)_2I_3$, in which the highly conducting plane is the $a$–$b$ plane, i.e., $k_z \parallel c$. The functions $1_{\mathbf{k}}$, $X_{\mathbf{k}}$, $Y_{\mathbf{k}}$, $Z_{\mathbf{k}}$, $A_{\mathbf{k}}$, $B_{\mathbf{k}}$ and $C_{\mathbf{k}}$ may be any functions which transform, respectively, as 1, $k_x$, $k_y$, $k_z$, $k_a$, $k_b$ and $k_c$ under the operations of the group and satisfy translational symmetry.

| Irrep | Required nodes | Example basis functions ($k_z \parallel b$) | States | Example basis functions ($k_z \parallel c$) | States |
|---|---|---|---|---|---|
| $A_{1g}$ | None | $1_{\mathbf{k}}$, $A_{\mathbf{k}}^2$, $B_{\mathbf{k}}^2$, $C_{\mathbf{k}}^2$, $X_{\mathbf{k}}Y_{\mathbf{k}}$ | s, $d_{xy}$ | $1_{\mathbf{k}}$, $X_{\mathbf{k}}Y_{\mathbf{k}}$, $1_{\mathbf{k}} + X_{\mathbf{k}}Y_{\mathbf{k}}$ | s, $d_{xy}$ |
| $B_{1g}$ | Line | $A_{\mathbf{k}}B_{\mathbf{k}}$, $(X_{\mathbf{k}} + Y_{\mathbf{k}})Z_{\mathbf{k}}$ | $d_{(x+y)z}$ | $A_{\mathbf{k}}B_{\mathbf{k}}$, $X_{\mathbf{k}}^2 - Y_{\mathbf{k}}^2$ | $d_{x^2-y^2}$ |
| $B_{2g}$ | Line | $A_{\mathbf{k}}C_{\mathbf{k}}$, $X_{\mathbf{k}}^2 - Y_{\mathbf{k}}^2$ | $d_{x^2-y^2}$ | $A_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} + Y_{\mathbf{k}})Z_{\mathbf{k}}$ | $d_{(x+y)z}$ |
| $B_{3g}$ | Line | $B_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} - Y_{\mathbf{k}})Z_{\mathbf{k}}$ | $d_{(x-y)z}$ | $B_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} - Y_{\mathbf{k}})Z_{\mathbf{k}}$ | $d_{(x-y)z}$ |

these results strongly suggest that conventional 's-wave' pairing (which transforms like the trivial irreducible representation) is *not* realized in these materials. Triplet states can be ruled out [20] on the basis of measurements of the Knight shift [15] and upper critical field [27].

$\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$ have orthorhombic ($D_{2h}$) crystal structures (see figure 2). There are four even parity irreducible representations of $D_{2h}$ (see table 1) all of which are one dimensional. Canonically, the highly conducting plane is the $ac$ plane in both $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$. Further, it is usual to define the $x$ and $y$ axes as lying along the directions of the largest inter-dimer hopping integrals, which lie along the diagonals of the $ab$ plane so that $\hat{\mathbf{x}} = (\hat{\mathbf{b}} + \hat{\mathbf{c}})/2$ and $\hat{\mathbf{y}} = (\hat{\mathbf{b}} - \hat{\mathbf{c}})/2$ (see figure 2).

The organic superconductors are extremely anisotropic: the inter-plane hoping integral is about three orders of magnitude smaller than that in-plane [5]. The superconducting properties are also extremely anisotropic [4]. Hence, superconductivity in which the order parameter transforms as either the $B_{1g}$ or $B_{3g}$ irreducible representations are unlikely [3]. Therefore, a '$d_{x^2-y^2}$' state transforming as the $B_{2g}$ irreducible representation of $D_{2h}$ is most consistent with the experimental evidence.

$\kappa$-$(ET)_2Cu(NCS)_2$ has a monoclinic crystal structure (see figure 1) with the symmetry of the $C_{2h}$ point group and the highly conducting plane is the $bc$ plane. Here, the $x$ and $y$

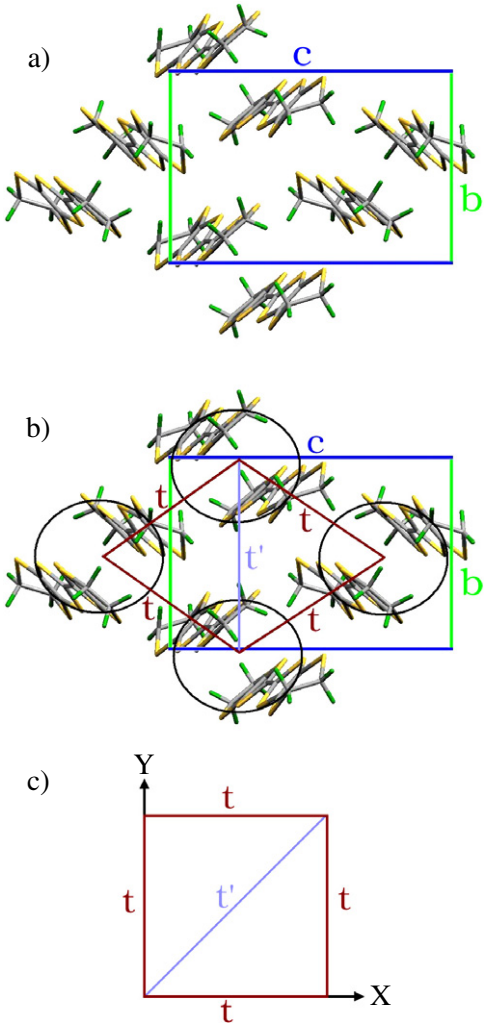


**Figure 2.** An anisotropic triangular lattice provides a simple model of the band structure of the organic charge transfer salts. Panel (a) shows the arrangement of ET molecules in the *bc* plane of $\kappa$-$(ET)_2Cu(NCS)_2$. Panel (b) shows the dimerization of the molecules and the largest inter-dimer hopping integrals. Panel (c) shows the anisotropic triangular lattice. Note that the crystallographic axes in (b) and not parallel to the $x$ and $y$ axes in panel (c): this is typical of organic charge transfer salts. The symmetry of this model is $C_{2v}$ as it is symmetric under the identity, rotation by $\pi$ about the $z$ axis, and reflection through either diagonal of the $xy$ plane. However, this is not the symmetry of the actual materials as is illustrated in figure 1.

axes are usually taken to be along the diagonals of the *bc* plane (see figure 2). The only non-identity irreducible representation of $C_{2h}$ that corresponds to singlet superconductivity is $B_g$ (see table 2). This has symmetry required nodes only along the *c* axis.

However, a subset of the possible choices for the basis function of the $B_g$ irreducible representation lead to '$d_{x^2-y^2}$' superconductivity (i.e., states with nodes along $k_x^2 = k_y^2$), which we have just argued is the superconducting state realized in $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$. Further, the properties of $\kappa$-$(ET)_2Cu(NCS)_2$ are so similar to those of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ that the differences between the two materials are often described

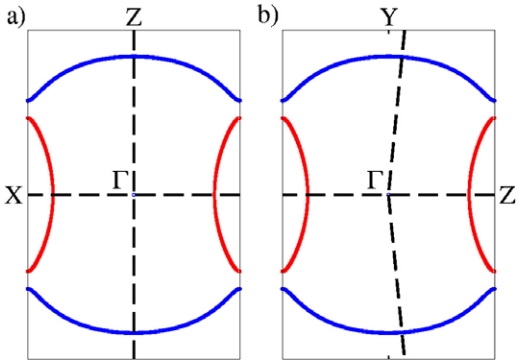


**Figure 3.** Comparison of the symmetry of the '$d_{x^2-y^2}$-like' states in (a) $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and (b) $\kappa$-$(ET)_2Cu(NCS)_2$. Panel (a) shows state which transforms like the $B_{2g}$ irreducible representation of $D_{2h}$. This has symmetry required nodes along the lines Γ–Z and Γ–X. Panel (b) shows a state that transforms according to the $B_g$ irreducible representation of $C_{2h}$. This has only one symmetry required node: along the line Γ–Z. If additional nodes do occur they will be formally accidental and are not required to lie in any particular crystallographic direction. One possible choice of additional node is shown.

**Table 2.** The symmetry required nodes of the even parity irreducible representations of the group $C_{2h}$ which represents the symmetry of $\kappa$-$(ET)_2Cu(NCS)_2$ and several other charge transfer salts with monoclinic unit cells. Note that the symmetry line node in the $B_g$ irreducible representation is required to lie in the plane $k_c = k_x - k_y = 0$.

| Irrep | Required nodes | Example basis functions | States |
|---|---|---|---|
| $A_g$ | None | $1_{\mathbf{k}}$, $A^2_{\mathbf{k}}$, $B^2_{\mathbf{k}}$, $C^2_{\mathbf{k}}$ | s, $d_{xy}$ |
| $B_g$ | Line | $A_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} - Y_{\mathbf{k}})Z_{\mathbf{k}}$, $B_{\mathbf{k}}C_{\mathbf{k}}$, $X^2_{\mathbf{k}} - Y^2_{\mathbf{k}}$ | $d_{x^2-y^2}$, $d_{(x-y)z}$ |

as 'chemical pressure' [7][3]. Therefore, one expects that the superconducting states of the two materials are closely related. If the node is shifted away from the *b* axis in the higher symmetry, orthorhombic, case (as sketched in figure 3) then there is a change in symmetry which is accompanied by a phase transition. There is no requirement for such as phase transition in the monoclinic case as both possible the order parameters shown in figure 3 transform as the $B_g$ irreducible representation of $C_{2h}$. Any finite contribution to the superconducting order parameter from basis functions which do not have nodes along *b* axis will cause this node to move or, for a sufficiently large contribution, disappear. Thus, predictions or measurements which show that monoclinic materials have nodes anywhere except along the *c* axis are not robust. Therefore one cannot conclude that the 'd-wave' ($B_g$) state is '$d_{x^2-y^2}$'. If there is an accidental node then it will not lie along *b* axis and it may have either a temperature dependence, a $k_z$ dependence or both.

Another interesting possibility is that of what might be termed '$s + d_{xy}$' superconductivity in $\kappa$-$(ET)_2Cu(NCS)_2$. This state must transform according to the trivial $A_g$ irreducible representation, but could have a large component which would transform like the $d_{xy}$ function on the square lattice and thus have accidental nodes close to $k_x \sim 0$ and $k_y \sim 0$. This would be consistent with measurements of thermal conductivity [28] and tunnelling spectra [26]. However, both of these experiments remain controversial: no coherence peaks are observed

[3] The chemical pressure hypothesis is that the main effect when the anion varied is the change in unit cell volume.

in the tunnelling spectra and so one cannot be sure that surface effects do not dominate these experiments; and the anisotropy observed by Izawa *et al* [28] is extremely small and has the full symmetry of the lattice and therefore it is not clear that this results from the superconductivity (see [6] for a fuller discussion of these experiments). Note however, that a pure '$d_{xy}$' (which has discussed in the context of several experiments [26, 28]) is not symmetry distinct state in $\kappa$-$(ET)_2Cu(NCS)_2$ and is therefore *not* a possibility. An '$s + d_{xy}$' state would also explain why Analytis *et al* [25] were unable to completely suppress superconductivity in their irradiation experiments. However, one cannot identify the superconducting state of $\kappa$-$(ET)_2Cu(NCS)_2$ as '$s + d_{xy}$' without an adequate explanation of why no Hebel–Schlicter peak is observed. Clearly more experiments are need to differentiate between the $A_g$ and $B_g$ scenarios but this work at least provides the terms in which these experiments should be interpreted.

The above arguments also show that calculations based on the anisotropic triangular lattice [6, 8, 19, 22, 23, 29] (whose symmetry is represented by the group $C_{2v}$) exclude components of the gap in a manner that is not relevant to the monoclinic materials. Thus weak interactions excluded by these models will dramatically change the symmetry of the gap. Even neglecting such interactions, at sufficiently low temperatures at least small additional '$d_{(x-y)z}$' or 's' components to the order parameter are expected. Exotic states with more nodes than are present in '$d_{x^2-y^2}$' states have been proposed [30]. Such nodes would almost certainly be lifted in both monoclinic and orthorhombic materials as they are far from robust.

Note that it is not the approximations made in these calculations [6, 8, 19, 22, 23, 29, 30], that cause the incorrect symmetry to be predicted, but rather the oversimplified models of the band structure. In particular the models of the band structure used in many calculations have a different symmetry than that realized in the actual materials. To illustrate this we sketch a commonly used model band structure (the anisotropic triangular lattice) in figure 2 and show the unit cells of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu(NCS)_2$ in figure 1. It is clear from even the briefest examination of these figures that the anisotropic triangular lattice has significantly different symmetry than either the unit cell of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ or $\kappa$-$(ET)_2Cu(NCS)_2$.

*Time reversal symmetry breaking in* $\kappa$-$(ET)_2Cu_2(CN)_3$ *and* $\beta'$-$[Pd(dmit)_2]_2X$. Much attention [14] has been focused on $\kappa$-$(ET)_2Cu_2(CN)_3$ following the discovery that, in spite of there existing well formed local moments, in the low pressure, insulating phase, these moments do not order down to the lowest temperatures studied (32 mK) [11]. Both Huckel calculations [31] and fits of the susceptibility calculated by series expansions [11, 32] to that observed experimentally suggest that the band structure of $\kappa$-$(ET)_2Cu_2(CN)_3$ is well approximated by that of the isotropic triangular (or more correctly hexagonal) lattice. Series expansions [12, 32] also show that the hexagonal lattice Heisenberg model is a good approximation for the low pressure, insulating phase of $\beta'$-$[Pd(dmit)_2]_2X$. The success of these simple models implies that the normal state has an approximate $C_{6v}$ or $C_{6h}$ symmetry. Therefore, it is useful to consider the superconducting states in materials with approximate $C_{6v}$ ($C_{6h}$) symmetry, and then include terms which lower the symmetry to that of the true crystal perturbatively.

An interesting feature of $C_{6v}$ ($C_{6h}$) is that 'd-wave' states transform according to a two-dimensional (2D) irreducible representation, $E_{2(g)}$. In a 2D irreducible representation the order parameter, $\Delta_{\mathbf{k}}$, is a linear combination of the basis functions, $\Psi_{\mathbf{k}}^{1,2}$, of the irreducible representation, i.e., $\Delta_{\mathbf{k}} = \eta_1\Psi_{\mathbf{k}}^1 + \eta_2\Psi_{\mathbf{k}}^2$. Hence, on the hexagonal lattice the Ginzburg–Landau free energy of order parameters belonging to the 2D irreducible representations is [2, 3]

$$F_s - F_n = \alpha(T - T_c)(|\eta_1|^2 + |\eta_2|^2) + \beta_1(|\eta_1|^2 + |\eta_2|^2)^2 + \beta_2(\eta_1^*\eta_2 - \eta_1\eta_2^*)^2. \quad (1)$$

The ground state solution, $\vec{\eta} = (\eta_1, \eta_2)$, is: (i) $\vec{\eta} = (1, 0)$ or (ii) $\vec{\eta} = (0, 1)$ for $\beta_2 > 0$ (the degeneracy is lifted by sixth order terms [2, 3]); (iii) $\vec{\eta} = (1, i)$ for $\beta_2 < 0$ (this is the weak

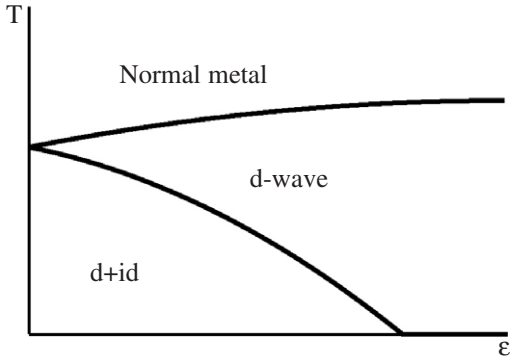


**Figure 4.** Sketch of the predicted phase diagram for superconductivity in systems whose band structure is close to that of the hexagonal lattice such as $\kappa$-$(ET)_2Cu_2(CN)_3$ and $\beta'$-$[Pd(dmit)_2]_2X$. $\varepsilon$ is a symmetry breaking parameter which lowers the symmetry from $C_{6v}$ to $C_{2h}$. Physically $\varepsilon$ could represent uniaxial strain or pressure. $\varepsilon \neq 0$ at ambient pressure due to the monoclinic crystal structure.

coupling solution). In the $E_{2(g)}$ irreducible representation $\Psi^1_{\mathbf{k}}$ describes a '$d_{x^2-y^2}$' state and $\Psi^2_{\mathbf{k}}$ describes a '$d_{xy}$' state. Thus the three solutions correspond to (i) '$d_{x^2-y^2}$' superconductivity; (ii) '$d_{xy}$' superconductivity; and (iii) '$d_{x^2-y^2} + i\,d_{xy}$' superconductivity. Thus state (i) is the same state as we have discussed above for the orthorhombic materials. However, a number of studies [33] of superconductivity on the hexagonal lattice suggest that state (iii) is realized.

*The role of monoclinicity.* It is important to realize that although the band structures of $\kappa$-$(ET)_2Cu_2(CN)_3$ and $\beta'$-$[Pd(dmit)_2]_2X$ are close to the hexagonal lattice, they will not be precisely that of the hexagonal lattice because these materials form monoclinic crystals. The monoclinic distortion of the crystal lowers the symmetry of the microscopic Hamiltonian. As we as changing perturbing the d-wave states in the same way as occurs in $\kappa$-$(ET)_2Cu(NCS)_2$ significant new effects are introduced due the proximity to the triangular lattice. We account for this perturbation by introducing a symmetry breaking field, $\varepsilon$ which, to lowest order, enters the free energy as $\varepsilon(|\eta_1|^2 - |\eta_2|^2)$ [34]. Thus,

$$F_s - F_n = \alpha_+|\eta_1|^2 + \alpha_-|\eta_2|^2 + \beta_1(|\eta_1|^2 + |\eta_2|^2)^2 + \beta_2(\eta_1^*\eta_2 - \eta_1\eta_2^*)^2, \quad (2)$$

where $\alpha_\pm = \alpha(T - T_{c\pm})$ and $T_{c\pm} = T_c \pm \varepsilon/\alpha$. This theory predicts that the monoclinic crystal will have two superconducting transitions, the first to either a $B_g$ ('$d_{x^2-y^2} + d_{(x-y)z}$') superconducting state or an $A_g$ ('$d_{xy} + s$') superconducting state (both of which have nodes) and the second to a, fully gapped, $A_g + iB_g$ ('$d + id$') state. This leads us to propose the phase diagram sketched in figure 4. For small $\varepsilon$ the difference in the two $T_c$s grows linearly with $\varepsilon$. But, for large $\varepsilon$ the symmetry of the lattice will cease to be related to that of $C_{6v}$ and return to that of $C_{2v}$. Therefore, for large $\varepsilon$ all of the irreducible representations are one dimensional and, neglecting the possibility of accidental degeneracies, we expect a single superconducting transition. A similar scenario has previously been studied in some detail in the context of the double superconducting transition observed in $UPt_3$ [34]. However, for $UPt_3$ the proposed symmetry breaking field arises from a weak antiferromagnetic background [2], rather than from the crystal structure.

The above predictions are readily testable. Any number of experiments might see the double superconducting transition (e.g., specific heat or ultrasound). Further, the proposed low temperature '$d + id$' state breaks time reversal symmetry, this could be detected directly

**Table 3.** Summary of the superconducting states proposed on the basis of the group theoretical analysis in this work. The parenthetic point group and irreducible representation in the first row indicate the approximate symmetries which drive the physics.

| Point group | Example material | Irrep | State |
|---|---|---|---|
| $C_{2h}$ ($C_{6h}$) | $\kappa$-$(ET)_2Cu_2(CN)_3$ | $B_g + iA_g$ ($E_{2g}$) | 'd + id' |
| $D_{2h}$ | $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ | $B_{2g}$ | '$d_{x^2-y^2}$' |
| $C_{2h}$ | $\kappa$-$(ET)_2Cu(NCS)_2$ | $B_g$ | '$d_{x^2-y^2}$ + d' |
| $D_{2h}$ | $\theta$-$(ET)_2I_3$ | $A_{1g}$ | '$d_{xy}$ + s' |
| $C_i$ | $\beta''$-$(ET)_2SF_5CH_2CF_2SO_3$ | $A_g$ | '$d_{xy}$ + s' |

by a number of experiments [2] most notably $\mu$SR[4]. Experimental confirmation of a double superconducting transition and broken time reversal symmetry would be extremely important, not only because of the intrinsic interest in these phenomena, but also because they would be conclusive proof of unconventional superconductivity in the layered organic superconductors. An important caveat on this prediction is that the requisite experiments to test for triplet superconductivity in $\kappa$-$(ET)_2Cu_2(CN)_3$ have not yet been reported. There are strong ferromagnetic fluctuations on the triangular lattice [18], thus triplet superconductivity is a possibility. However, the above analysis is equally applicable to the $E_{1(u)}$ irreducible representation which corresponds to a $A_u + iB_u$ ('p + ip') state.

*Undimerized materials* have been less studied experimentally, but, measurements of the in-plane and inter-plane penetration depths show power law dependences suggesting unconventional superconductivity [36]. Some undimerized organic superconductors, e.g., $\theta$-$(ET)_2I_3$, have unit cells with a $D_{2h}$ point group, while others, e.g., $\beta''$-$(ET)_2SF_5CH_2CF_2SO_3$, have $C_i$ point groups. Many theoretical models of these materials have assumed that the materials have a square lattice. (Note that the unit cell used in this model is again rotated with respect to the crystallographic unit cell so that $\hat{\mathbf{x}} = (\hat{\mathbf{a}} + \hat{\mathbf{b}})/2$ and $\hat{\mathbf{y}} = (\hat{\mathbf{a}} - \hat{\mathbf{b}})/2$.) Calculations based on square lattice models have led to the idea that charge and spin fluctuations may cooperatively mediate '$d_{xy}$' superconductivity [16] i.e., the that the order parameter transforms like the $B_2$ irreducible representation of $C_{4v}$. However, this prediction of the location of the nodes is not robust as the crystal lattices have significantly lower symmetries than the model. In the $D_{2h}$ point group (table 1) the basis functions that describe the '$d_{xy}$' superconducting state belong to the trivial $A_{1g}$ irreducible representation. Therefore, these nodes are not robust in the same sense as '$d_{x^2-y^2}$' states are not robust in monoclinic crystals. Thus one expects that the undimerized materials will have an '$d_{xy}$ + s' order parameter. The order parameter may still have accidental nodes, but such nodes will be shifted away from the lines $k_x k_y = 0$. The same arguments and conclusions hold for undimerized materials with $C_i$ point groups. A similar argument suggested that cuprates with a small orthorhombic distortion are '$s + d_{x^2-y^2}$' superconductors [37]. Tunnelling experiments have shown that the order parameter of YBCO does indeed have a significant s-wave component [38].

In conclusion, we have presented a group theoretical analysis of several organic superconductors. This analysis has led us to propose order parameters summarized in table 3. However, we stress that these materials are examples of much wider classes. It is probable that the results in this work hold across these classes.

This work was motivated by conversations with J Annett and R McKenzie. It is a pleasure to thank A Ardavan, S Blundell, B Braunecker, A Carrington, A Doherty, J Fjærestad, M Lüders,

[4] For example Luke *et al* [35] performed just this kind of experiment to detect broken time reversal symmetry in the superconducting phase of $Sr_2RuO_4$.

J Merino, F Pratt, and J Varghese for useful conversations and R McKenzie for a critical reading of the manuscript. I thank ISIS, and the Universities of Bristol and Oxford for hospitality. This work was funded by the Australian Research Council.

*Note added*. Since this work was first placed on the arxiv, results supporting the prediction of a double superconducting transition and broken time reversal symmetry in materials near the triangular lattice have been derived from the resonating valence bond theory [39].

## References

[1] Volovik G E and Gor'kov L P 1985 *Sov. Phys.—JETP* **61** 843
[2] See, e.g. Sigrist M and Ueda K 1991 *Rev. Mod. Phys.* **63** 239 and references therein
[3] See, e.g. Annett J F 1990 *Adv. Phys.* **39** 83
[4] See, e.g. Ishiguro T, Yamaji K and Saito G 1998 *Organic Superconductors* (Heidelberg: Springer)
[5] For a recent review see Singleton J, McDonald R D and Harrison N 2006 *Preprint* cond-mat/0606492
[6] Powell B J and McKenzie R H 2006 *J. Phys.: Condens. Matter* **18** R827
[7] Kanoda K 1997 *Physica* C **282–287** 299
[8] Powell B J and McKenzie R H 2005 *Phys. Rev. Lett.* **94** 047004
[9] Pratt F L *et al* 2003 *Polyhedron* **22** 2307
Pratt F L and Blundell S J 2005 *Phys. Rev. Lett.* **94** 097006
Powell B J and McKenzie R H 2004 *J. Phys.: Condens. Matter* **16** L367
[10] Kagawa F, Miyagawa K and Kanoda K 2005 *Nature* **436** 534
[11] Shimizu Y *et al* 2003 *Phys. Rev. Lett.* **91** 107001
[12] Tamura M and Kato R 2002 *J. Phys.: Condens. Matter* **14** L729
[13] Merino J and McKenzie R H 2000 *Phys. Rev.* B **61** 7996
[14] For a review see Shimizu Y *et al* 2005 *Prog. Theor. Phys. Suppl.* **159** 52
[15] For a review see Miyagawa K, Kanoda K and Kawamoto A 2004 *Chem. Rev.* **104** 5635
[16] Merino J and McKenzie R H 2001 *Phys. Rev. Lett.* **87** 237002
McKenzie R H *et al* 2001 *Phys. Rev.* B **64** 085109
Greco A *et al* 2005 *Phys. Rev.* B **71** 144502
[17] McKenzie R H 1997 *Science* **278** 820
[18] Merino J, Powell B J and McKenzie R H 2006 *Phys. Rev.* B **73** 235107
[19] For a review see Kuroki K 2006 *J. Phys. Soc. Japan* **75** 051013
[20] For a review see Powell B J and McKenzie R H 2004 *Phys. Rev.* B **69** 024519
[21] See, e.g. Damascelli A, Hussain Z and Shen Z-X 2003 *Rev. Mod. Phys.* **75** 473
[22] Hotta C 2003 *J. Phys. Soc. Japan* **72** 840
[23] Kino H and Fukuyama H 1996 *J. Phys. Soc. Japan* **65** 2158
[24] Carrington A *et al* 1999 *Phys. Rev. Lett.* **83** 4172
Elsinger H *et al* 2000 *Phys. Rev. Lett.* **84** 6098
Müller J *et al* 2002 *Phys. Rev.* B **65** 140509(R)
[25] Analytis J G *et al* 2006 *Phys. Rev. Lett.* **96** 177002
[26] Ichimura K and Nomura K 2006 *J. Phys. Soc. Japan* **75** 051012
[27] Zuo F *et al* 2000 *Phys. Rev.* B **61** 750
[28] Izawa K, Yamaguchi H, Sasaki T and Matsuda Y 2002 *Phys. Rev. Lett.* **88** 27002
[29] Liu J, Schmalian J and Trivedi N 2005 *Phys. Rev. Lett.* **94** 127003
Gan J Y *et al* 2005 *Phys. Rev. Lett.* **94** 067005
[30] See, e.g. Schmalian J 1998 *Phys. Rev. Lett.* **81** 4232
[31] Komatsu T *et al* 1996 *J. Phys. Soc. Japan* **65** 1340
[32] Zheng W *et al* 2005 *Phys. Rev.* B **71** 134422
[33] Ogata M 2003 *J. Phys. Soc. Japan* **72** 1839
Honerkamp C 2003 *Phys. Rev.* **68** 104510
Kumar B and Shastry B S 2003 *Phys. Rev.* B **68** 104508
Baskaran G 2003 *Phys. Rev. Lett.* **91** 097003
Braunecker B, Lee P A and Wang Z 2005 *Phys. Rev. Lett.* **95** 017004
[34] Hess D W, Tokuyasu T A and Sauls J A 1989 *J. Phys.: Condens. Matter* **1** 8135
Machida K, Ozaki M and Ohmi T 1989 *J. Phys. Soc. Japan* **58** 4116
[35] Luke G M *et al* 1998 *Nature* **394** 558

[36] Prozorov R *et al* 2001 *Phys. Rev.* B **63** 052506
[37] Sigrist M *et al* 1996 *Phys. Rev.* B **53** 2835
[38] Kouznetsov K A *et al* 1997 *Phys. Rev. Lett.* **79** 3050
[39] Powell B J and McKenzie R H 2006 *Preprint* cond-mat/0607079