Eur. Phys. J. B **4**, 409–411 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Rapid Note

On the Fermi surface of some organic superconductors with sizeable critical temperatures

J. Friedel

Laboratoire de Physique des solides[a], Université Paris-Sud, Centre d'Orsay, 91405 Orsay Cedex, France

Received: 28 April 1998 / Revised and accepted: 13 May 1998

Abstract. Recent studies of the Fermi surface of quasi-two-dimensional organic conductors comfort the idea that the presence of a van Hove anomaly near the Fermi level is a favourable factor for superconductivity.

PACS. 74.70.Kn Organic superconductors – 74.25.Jb Electronic structure

Beckmann *et al.* [1] have recently reported measurements of the Fermi surface of an organic superconductor with a fairly high T_c: $\beta''-(ET)_2SF_5CH_3CF_2SI_3$ ($T_c \simeq 5.2$ K). The study shows the presence, in this quasi-two-dimensional compound, of fairly small pockets of rather free holes (Fig. 1). This agrees with the prediction of band structure computations [2], where the small pockets are due to the interaction of large interpenetrating Fermi cylinders of nearly free electrons. As usual in such cases, the interaction between cylinders replaces the branches AA' and BB' of the intersecting and nearly circular surfaces by a topology AB and $A'B'$ where closed holes pockets and parallel cylinders with wavy indefinite sections alternate. The computed band structures and the smallness of the interaction point however to the presence, at an energy near to the Fermi level, of a *van Hove anomaly* where two branches such as AA', BB' actually cross each other. When the energy moves further away from the Fermi level, the topology of the interaction changes to AB' and $A'B$, leading to couples of large electron loops.

It was already pointed out [3] that a similar van Hove anomaly presents itself near the Fermi level of the quasi-two-dimensional organic superconductor with one of the highest observed T_c ((BEDT-TTF)$_2$Cu(NCS)$_2$, with $T_c \simeq 10.4$ K, *cf.* [4,5]). Finally a recent study of the two high temperature phases of a third quasi-two-dimensional organic superconductor with more modest T_c ((BEDO-TTF)$_2$ReO$_4$H$_2$O, with $T_c \simeq 3$ K $\pm$ 0.5 K, [6]) exhibits very similar pockets at Fermi level: due to small interactions of intersecting cylinders with elliptical sections; they lead again to van Hove anomalies not far from the Fermi level.

The presence of such a quasi-two-dimensional van Hove anomaly near the Fermi level has also been observed in most high T_c oxide superconductors [3]. And it has been repeatedly pointed out that, in a classical weak coupling BCS situation, the peak in the density of electronic states associated with the van Hove anomaly can lead to substantial values of T_c if the Fermi level is near enough to the peak of the van Hove anomaly [7–9].

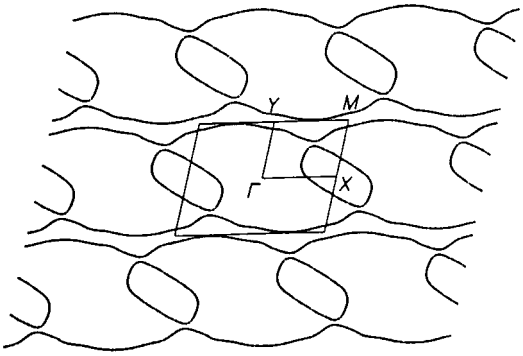

Fig. 1. Fermi surface of $\beta''-$(BEDT-TTF)$_2$SF$_5$CF$_2$SO$_3$ (after Ref. [1]).

Indeed, for s coupling, the mean field (two-dimensional) superconductive temperature T_2 is given by

$$\frac{2}{V} = \int_{E_F - k_B T_B}^{E_F + k_B T_D} \tanh\left(\frac{E - E_F}{2k_B T_2}\right) n(E) \frac{dE}{E - E_F} \qquad (1)$$

leading to a maximum value of T_2 for E_F at the van Hove anomaly, where the density of states $n(E)$ has a logarithmic infinity. V is here the coupling responsible for superconductivity and T_D the Debye temperature. T_2 is actually higher than the real (three-dimensional) critical temperature T_c, due to the fluctuations of the $(2d)$ order parameter. However as soon as the $3d$ couplings are sizeable, these fluctuations are much reduced and do not influence the order of magnitude of T_c (*cf.* for instance [3]).

[a] Unité associée au CNRS

Although fairly self-evident, the fair omnipresence of van Hove anomalies near the Fermi level in quasi-two-dimensional compounds has not been taken seriously by most people (*cf.* however *e.g.* [10,11]), for a variety of reasons that might be recalled.

1) It has often been stated that electron correlations are so strong in superconductive oxides that the details of the Fermi surface as predicted by independent electrons band computations should be lost and the van Hove anomalies washed out or strongly distorted. It is therefore of interest to see, in the organic superconductors, at least some cases where the band interactions responsible for the appearance of pockets of electrons and van Hove anomalies do subsist and corrections due to electron-electron interactions seem to remain modest. The same applies at least to some oxides such as Bi2212.

2) It has been argued [12] that strong electron-electron supraconductive couplings reduce appreciably the effect of van Hove anomalies. Although qualitatively self-evident, this does not change the order of magnitude of T_c. Furthermore, at least in the organic superconductors with moderate T_c's, it is not at all necessary for the superconductive couplings to be strong.

3) It is now established that, in oxide superconductors, the supraconductive gap is strongly anisotropic [13], although the exact nature of anisotropy is not yet completely clear and might vary from case to case: the presence of antiferromagnetic fluctuations suggests a d coupling [14], but an extended s coupling has also been suggested [15,16]. In organic superconductors, the presence of antiferromagnetic phases has also suggested a superconductive coupling through AF fluctuations [17], although, as far as I know, no systematic exploration of gap anisotropy has been made so far.

For electron coupling symmetry other than s, equation (1) for T_2 must be replaced by a more complex one, taking into account that the coupling potential V is now k dependant and the corresponding superconductive gap anisotropic. There is then a special case where the gap vanishes at the van Hove singularity point by symmetry; this is however *not* the case for any of the superconductors mentioned here. The van Hove anomaly should then reinforce the corresponding gap, T_2 and T_c in a way similar to that for s coupling. This point has only been clarified for explicit models [14,18] and could be usefully explored numerically for other cases and especially other gap symmetries.

4) T_2, and thus T_c, as deduced from equation (1) or their extension for anisotropic couplings, are not much influenced by various perturbations. This is due to the fact that, with the Lorentzian form of (1), it is the *wings* of the van Hove anomaly that matter and not its core [3,19]. This well-known fact allows to deduce a simple exponential form for T_2 from equation (1). But other physical consequences follow:

- T_c is not sensitive to the fact that the electrons in the core of the van Hove anomaly have low speeds (because $\nabla_k E = 0$ at the anomaly) and the usual assumptions for BCS couplings no longer hold [20].
- T_c is not much sensitive to small core corrections such as due to a weak warping of the cylinders of constant energy by $3d$ couplings [3], as indeed exists in most of the cases considered.
- T_c decreases only slowly from its maximum value when the Fermi level shifts from the peak of the van Hove anomaly by amounts of the order of the width of the core of the anomaly. Typically, the decrease with doping is slower than that of the Néel temperature of an AF phase. This helps to explain why superconductivity can appear in oxides for doping larger than for AF phases or than for strong AF fluctuations responsible for a magnetic pseudogap effect [19]. It means that the van Hove anomaly does not have necessarily its peak at the Fermi level for the doping giving the maximum of T_c, as often assumed when discussing its possible effect in oxide superconductors (*cf.* [10,18] for instance); the position of the van Hove anomaly might well be then for definitely smaller dopings, where T_c is decreased by the development of a magnetic pseudogap [13].

In conclusion, the presence of a van Hove anomaly near the Fermi level of quasi-two-dimensional superconductors seems as frequent in organic as in oxide compounds. In all cases, it can help to explain moderate to high values of T_c, whether the gap is isotropic or anisotropic. The effect should, in fact, be little sensitive to the exact nature and symmetry of the superconductive coupling. More systematic studies of the effects of these van Hove anomalies on the properties of the normal phase would help to clarify this field of research. It might be useful for instance to point out that the presence of van Hove anomalies at the Fermi level of quasi-two-dimensional compounds leads to the same sort of extrastability as in $3d$ Hume Rothery phases, whether in crystals, quasicrystals or liquids [21,22].

References

1. D. Beckmann, S. Wanka, J. Wosnitza, J.A. Schlueter, J.M. Williams, P.G. Nixon, R.W. Winter, G.L. Gard, J. Ren, M.H. Whangbo, Eur. Phys. J. B **1**, 295 (1998).
2. U. Geiser, J.A. Schlueter, H.H. Wang, A.M. Kim, J.M. Williams, P.P. Sche, H.I. Zakowicz, M.L. van Zille, J.D. Dudek, P.G. Nixon, R.W. Winter, G.L. Gard, J. Ren, M.H. Whangbo, J. Am. Chem. Soc. **118**, 9996 (1996).
3. J. Friedel, J. Phys. Condens. Matter. **1**, 7757 (1989).
4. H. Uramaya, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, S. Tanaka, Chem. Lett. **55**, 100 (1988).
5. K. Oshima, T. Mori, H. Inokuchi, H. Uramaya, H. Yamochi, G. Saito, Phys. Rev. B **38**, 938 (1988).
6. K.S. Khasanov, B.Zh. Narymbetov, L.V. Zorina, L.P. Rozenberg, R.P. Shibaeva, N.D. Kushch, E.B. Yagubskii, R. Rousseau, E. Canadell, Eur. Phys. J. B **1**, 419 (1998).
7. J. Labbé, S. Barisic, J. Friedel, Phys. Rev. Lett. **19**, 1039 (1967).
8. J.E. Hirsch, D.J. Scalapino, Phys. Rev. Lett. **56**, 2732 (1986).

9. J. Labbé, J. Bok, Europhys. Lett. **3**, 1225 (1987).
10. D.M. Newns, H.R. Krishnamurty, P.C. Paltnaik, C.C. Tsuei, C.C. Chi, C.L. Kane, Physica **186-188**, 801 (1993).
11. J. Bok, Physica C **209**, 107 (1993).
12. R. Combescot, Europhys. Lett. **40**, L99 (1989).
13. *cf.* for instance, G. Deutscher in *Gap symmetry and fluctuation in high T_c superconductors*, NATO Advanced study Institute Cargèse 1997, edited by J. Bok, D. Pavuna (Plenum Press London, 1998 under press).
14. D. Pines, in *Gap symmetry and fluctuation in high T_c superconductors*, NATO Advanced study Institute Cargèse 1997, edited by J. Bok, D. Pavuna (Plenum Press London, 1998 under press).
15. A.A. Abrikosov, Physica C **222**, 191 (1994).
16. J. Bok, J. Bouvier, Physics C **244**, 357 (1995).
17. C. Bourbonnais, L.G. Caron, Europhys. Lett. **5**, 209 (1988).
18. J. Bouvier, J. Bok, J. Supercond. **10**, 673 (1997).
19. J. Friedel, Physica C **153-155**, 1610 (1988).
20. E. Cappelhets, L. Pietronero, Europhysics Lett. **36**, 619 (1996).
21. A. Blandin, Alloying behaviour and concentrated solutions, edited by T.D. Massalsky (Gordon and Breach New York, 1965).
22. J. Friedel, Helv. Physica Acta **61**, 638 (1988).