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Physical Properties and Concepts for Organic Conductors

C. Bourbonnais,* F. Creuzet, P. Wzietek and D. Jerome

Laboratoire de Physique des Solides, Bat. 510, U.P.S., 91405 Orsay Cedex, France

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Abstract

In this short review we discuss the main differences observed in the physical properties of $(\text{TMTSF})_2\text{X}$ and $(\text{BEDT-TTF})_2\text{X}$ families of organic conductors. The special role played by quasi-one- or quasi-two-dimensionality in the magnetic and superconducting properties of these compounds is analyzed in the light of some recent experimental data.

1. Introduction

Organic conductors form a class of strongly anisotropic materials with a large variety of interesting properties [1]. For instance, the temperature-pressure phase diagram of the Bechgaard salts $(\text{TMTSF})_2\text{X}$ exhibits a common boundary between superconducting and antiferromagnetic phases [2]. In fact, the latter is closely related to the quasi one-dimensional nature of the electron gas and a lot of studies have been devoted to define the precise mechanism involved in the origin of this long range ordering. This is also the case for the sulfur analog $(\text{TMTTF})_2\text{X}$. This is an important step which has to be achieved in order to examine the possible role of antiferromagnetism spin fluctuations in the pairing mechanism responsible for superconductivity [3]. In the following short review, we shall present an interpretation of NMR results which give valuable information on the origin of correlations, their amplitude, dimensionality and temperature profile.

We shall discuss the essential differences between the Bechgaard salts and the quasi two-dimensional $(\text{BEDT-TTF})_2\text{X}$ series. Namely, these systems exhibit a much higher superconducting transition temperature T_c with a phase diagram that does not reveal any magnetic phase close to the superconducting one [1]. Furthermore, we shall briefly emphasize the consequences of the nuclear relaxation profile at the superconducting transition.

2. Electronic correlations and dimensionality in the Bechgaard salts

In the past few years a log of interest has been devoted to the study of electronic correlations in organic conductors by the use of nuclear spin-lattice relaxation measurement. With this technique, it is possible to probe both ferromagnetic and antiferromagnetic electronic correlations, since the local character of the hyperfine coupling between electrons and nuclei provides information on electronic spin fluctuations at all wavevectors q . This is well illustrated by the standard Moriya formula [4]:

$$T_1^{-1} = 2\gamma_N^2 |A|^2 T \int d^d q \chi''_{\perp}(q, \omega_N) / \omega_N \quad (1)$$

where γ_N is the gyromagnetic ratio of the nucleus, ω_N is the NMR frequency, A is the hyperfine coupling constant, and $\chi''_{\perp}(q, \omega_N)$ is the imaginary part of the retarded electronic susceptibility. In the case of the organic conductors considered here, this electronic contribution drives the nuclear relaxation; therefore, the analysis of the temperature T_1^{-1} profiles will permit to decide on the nature of electronic correlation associated with both ordered and disordered states.

First, let us consider the high temperature ($T > 30\text{ K}$) behavior of ^{77}Se relaxation rate in two typical Bechgaard salts, namely $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$ (Fig. 1) [5, 6]. We cannot recognize the Korringa-like relation ($T_1^{-1} \propto T$) usually found in ordinary uncorrelated metals. Instead, we observe a clear upward curvature which indicates that the enhancement of the relaxation, as evaluated with $(T_1 T)^{-1}$, increases with temperature. This is reminiscent of the temperature dependence of the uniform and static susceptibility χ_s . Indeed, Fig. 2 obtained with Faraday data of Miljak *et al.* [7], for χ_s , clearly shows that, in this temperature range, T_1^{-1} scales like $T\chi_s^2(T)$:

$$T_1^{-1} = C_0 T \chi_s^2(T) + C_1 \quad (2)$$

with $C_1 \approx 0$. It is well known that the Coulomb repulsion is responsible for the increase of the spin susceptibility at high temperature related to the existence of paramagnetic excitations (paramagnons). It has been shown that this kind of excitation imposes the following scaling relationship for

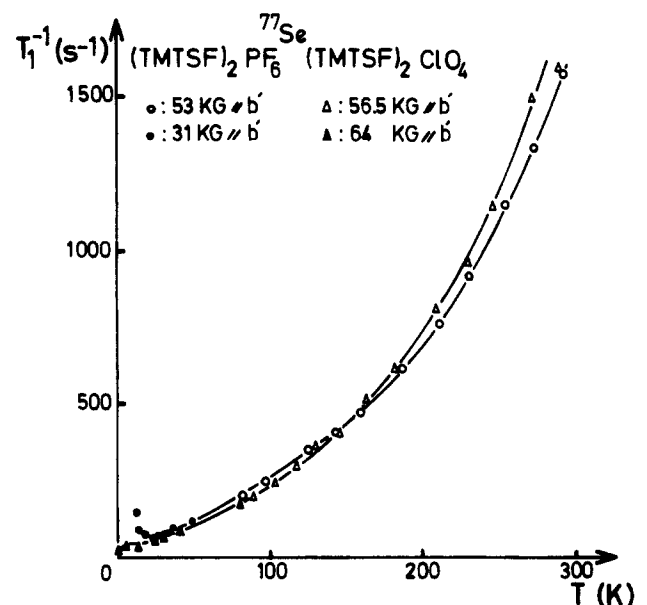


Fig. 1. ^{77}Se T_1^{-1} vs. T data of $(\text{TMTSF})_2\text{PF}_6$ (circles) and $(\text{TMTSF})_2\text{ClO}_4$ (triangles) at $P = 1$ bar. The full circles and triangles correspond to the low temperature Ref. [5] data of Creuzet *et al.* (Ref. [6]).

* Permanent address: Centre de Recherche en Physique du Solide, Dept. de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K-2R1.

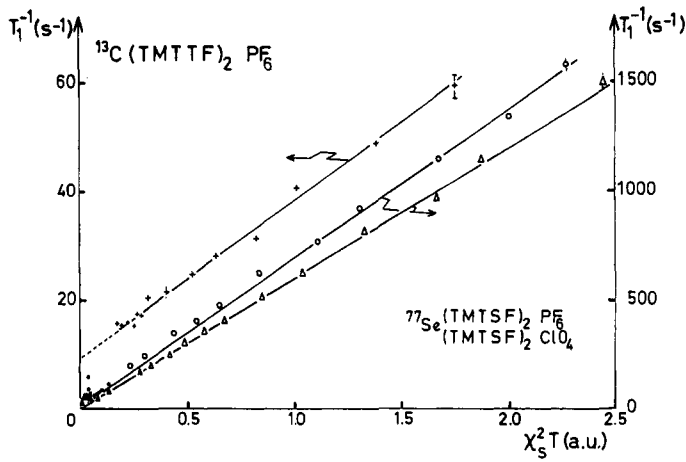


Fig. 2. ^{77}Se data of Fig. 1 vs. $\chi_s^2 T$ values of Miljak *et al.* (Ref. [7]) for $(\text{TMTSF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{ClO}_4$ (right scale). On the left scale, ^{13}C T_1^{-1} vs. EPR $\chi_s^2 T$ data of Creuzet *et al.* (Ref. [9]) for $(\text{TMTTF})_2\text{PF}_6$ at $P = 1$ bar and $H_0 = 42 \text{ Kg}/\text{C}^*$.

small q in eq. (1) [5]:

$$T_1^{-1}(q \sim 0) = C_0 T \chi_s^{(5-d)/2} \quad (3)$$

where d is the dimensionality of the system. Therefore, in the wide temperature domain where the law $T_1^{-1} \propto T \chi_s^2(T)$ is well obeyed, the experimental data support the existence of one-dimensional (1D) paramagnons [5]. We want to emphasize that the relation $T_1^{-1} \propto T \chi_s(T)$ is well known to be verified in 3D correlated materials such as intermetallic compounds [8].

It is well established that the $(\text{TMTSF})_2\text{X}$ and their sulfur analog $(\text{TMTTF})_2\text{X}$ series can develop antiferromagnetic long range order at low temperature [9, 10]. So, it is reasonable to expect an additional contribution to the relaxation rate from the staggered term in eq. (1). As an example, let us focus on the $(\text{TMTTF})_2\text{PF}_6$ data [9] displayed in Fig. 2 which strikingly show the existence of a temperature independent contribution to the relaxation between 40 K and 200 K. The resistivity minimum which occurs at $T_0 \cong 230 \text{ K}$ [10] indicates a 1D Mott-Hubbard localization which goes together with strong antiferromagnetic 1D fluctuations. Scaling analysis and direct calculations have shown that, in such a case, a power law divergence [7, 9] describes the enhancement of the ($q = 2k_F$) magnetic susceptibility [$\chi(q = 2k_F, T) \propto (T/T_0)^{-1}$]. The evaluation of eq. (1) for the $q \sim 2k_F$ terms leads to $T_1^{-1}(q \sim 2k_F) \propto T(T/T_0)^{-1} = C_1$, a temperature independent sizeable contribution. In $(\text{TMTSF})_2\text{X}$, the absence of localization is consistent with a much smaller amplitude of antiferromagnetic correlations at high temperature, as seen through the weakness of C_1 (Fig. 2).

At this point, it is interesting to compare the two contributions described above to the ones observed in the two-chain organic conductor $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ (Fig. 3) [11]. This compound remains metallic down to the lowest temperature ($T = 1.2 \text{ K}$) at ambient pressure. From Fig. 3, we can identify two different regimes of relaxation, one with an upward curvature above 100 K and the other with a downward curvature below 50 K. These features have been interpreted to respectively correspond to the $q = 0$ and $q = 2k_F$ magnetic fluctuations contributions to the relaxation. More precisely, the enhancement factor profile $(T_1 T)^{-1}$ develops a typical 1D

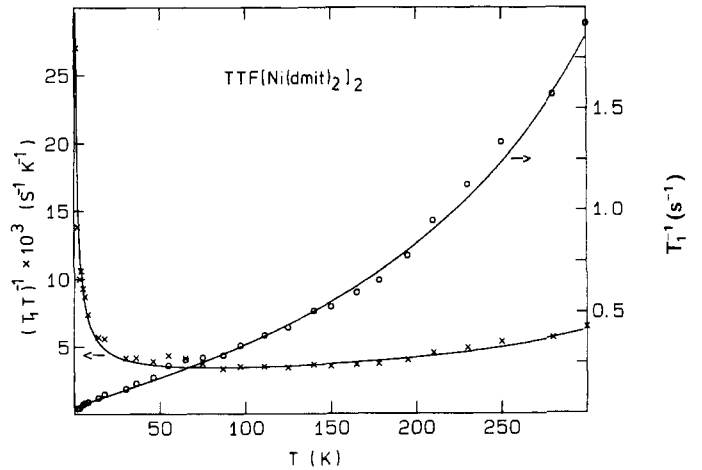


Fig. 3. Temperature dependence of ^1H T_1^{-1} (\square) and $(T_1 T)^{-1}$ (\times) for $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ at $P = 1$ bar and $H = 10.5 \text{ KG}$. After Wzietek *et al.* (Ref. [11]).

power law singularity at low temperature, showing that the system remains one dimensional in nature [11].

In the low temperature range from $(\text{TMTSF})_2\text{X}$, the growth of antiferromagnetic correlations becomes perceptible. For the PF_6 salt, the antiferromagnetic transition at $T_N = 12 \text{ K}$ is responsible for a singular behavior of T_1^{-1} (Fig. 4) which extends over a wide critical domain above T_N ($\Delta T_{\text{fluc}}/T_N \sim 1$) where $T_1^{-1} \propto (T - T_N)^{-1/2}$ [6a]. Such a critical behavior results from a 3D antiferromagnetic long range ordering. As pressure is applied, T_N is reduced and vanishes above a well defined critical pressure P_c ($\sim 6 \text{ kbar}$). Nevertheless, Fig. 4 gives a strong evidence for the presence of antiferromagnetic fluctuations that lead to a significant enhancement of the relaxation, down to 8 K or so. The same characteristic behavior is observed in the slowly cooled state of $(\text{TMTSF})_2\text{ClO}_4$ (Fig. 1) at ambient pressure [6b]. This common feature has

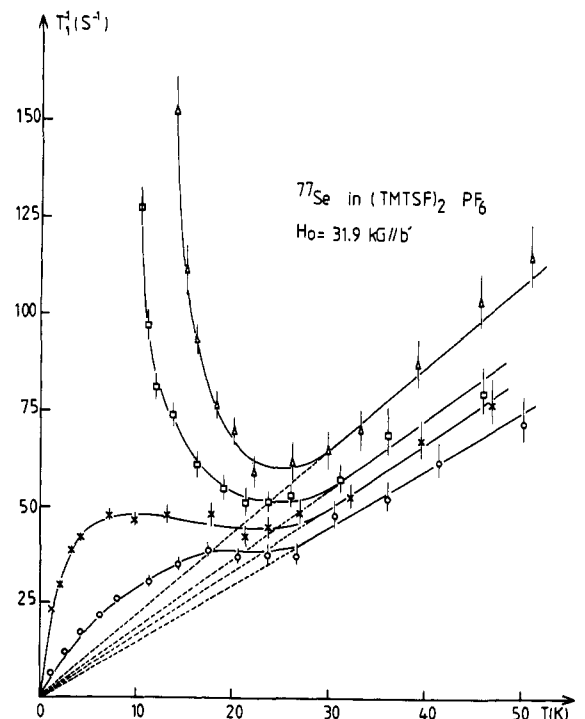


Fig. 4. ^{77}Se T_1^{-1} data vs. temperature in $(\text{TMTSF})_2\text{PF}_6$ at various pressure and low temperature. Δ : 1 bar; \square : 5.5 kbar; \times : 8 kbar; \circ : 11 kbar. After Ref. [6a].

been interpreted as the signature of the freezing of the divergence of the quasi-1D fluctuations that takes place at the dimensionality crossover temperature domain around $T_x = 8$ K. Below T_x , the transverse motion of the electrons is highly coherent and the detailed curvature of the Fermi surface becomes relevant for the description of the groundstate. However, the strong magnetic fluctuations developed above T_x have to be taken into account for a full understanding of the low temperature properties. In Ref. [12], the interchain exchange coupling has been shown to play a crucial role for the antiferromagnetic ordering at $P < P_c$ and for a large amplitude of the fluctuations at $P > P_c$ as well.

The existence of strong magnetic fluctuations above the superconducting transition described here obviously questions the pertinence of electron-phonon mechanism for superconductivity. The role of this BCS coupling can be ruled out by the absence of Peierls instability when magnetic field destroys superconductivity. For instance, it is well known that a magnetic phase is stabilized above a threshold field [13]. In fact, the kinetic exchange coupling between electrons on different stacks helps to avoid local Coulomb repulsion. It turns out that the resulting effective interaction between these electrons is attractive [12]. This new pairing mechanism can be seen as an exchange of antiferromagnetic quasi-1D paramagnons. As a consequence, the superconducting gap will have a line of zeros across the 3D open Fermi surface. Such a peculiar dependence will transform the Hebel-Slichter anomaly of T_1^{-1} into a power law decrease of the relaxation rate below T_c , as it has been experimentally confirmed in $(\text{TMTSF})_2\text{ClO}_4$ [14]. Note also that this interchain pairing is dramatically suppressed by non magnetic impurities and pressure [12], in good agreement with experiments [2].

3. $(\text{BEDT-TTF})_2\text{X}$: Quasi two dimensional organic superconductors

The first sulfur based organic superconductor $(\text{BEDT-TTF})_2\text{ReO}_4$ with $T_c = 2$ K at $P = 4$ kbar has drawn a lot of interest for the $(\text{BEDT-TTF})_2\text{X}$ family [15]. Since the early studies of this series, the structure of this class of material has suggested that the closer S-S contact in one of the transverse directions would give rise to a more pronounced 2D character of the electron gas, in contrast with the Bechgaard salts. The major breakthrough for organic superconductivity has been found in the I_3 salt with $T_c = 7.5$ K under a pressure of 1.5 kbar [16], a value which strikingly contrasts with the ambient pressure one of 1.5 K or so. This jump of T_c around 1.5 kbar is well understood in terms of a structural phase transition at 175 K which is related to an incommensurate modulation of the lattice [17]. The so called $(\beta\text{-H})$ unmodulated phase at $T > 175$ K is related to the highest T_c , while the lower T_c is related to the modulated $(\beta\text{-L})$ phase. Interestingly, the $(\beta\text{-H})$ phase can be stabilized at atmospheric pressure, provided that a well defined temperature-pressure cycling is followed. Then, the critical temperature for superconductivity can be raised up to 8.1 K at 1 bar (Fig. 5) [18]. As expected from the structure, the anisotropy of the transport properties reflects the quasi-2D character of the electronic spectrum ($\sigma_a/\sigma_b \sim 1$ and $\sigma_a/\sigma_c \sim 100$). This has been recently confirmed by the observation of Shubnikov de Haas oscillations when the field is oriented along the c axis [19]. Closed parts of the Fermi surface are also found as a

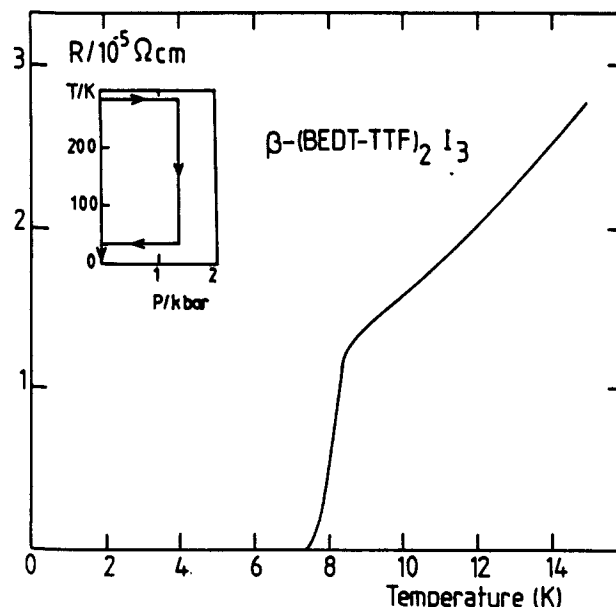


Fig. 5. Resistivity curve of the $\beta_{\text{H}}\text{-(BEDT-TTF)}_2\text{I}_3$ at $P = 1$ bar. In the insert, the pressure cycling process used to stabilize the β_{H} phase at low temperature. After Ref. [8].

result of band calculations [20]. The lack of antiferromagnetic transition in this material also strongly suggests the absence of good nesting of the Fermi surface. Nevertheless, infrared conductivity studies suggest that the Coulomb repulsion is quite relevant for the interpretation of the special character of the f sum rule [21].

^1H NMR investigations of the superconducting transition have revealed the occurrence of a giant peak of relaxation (Fig. 6), which is field dependent and seems to approach a sharp λ -like anomaly at zero field [21]. Furthermore, the relaxation rate below T_c is not activated and any field dependence could be detected below 4 K. From these results, it is clear that the whole picture of relaxation for $(\beta\text{-H})\text{-(BEDT-TTF)}_2\text{I}_3$ cannot be reconciled with the known NMR features resulting from the BCS model. Moreover, it has to be emphasized that these characteristics are quite different from the ones observed in the Bechgaard salts [14]. This is highly indicative of the need for a different starting point for the theoretical description of these compounds. More likely, the quasi-2D character of these systems must be considered as a basic ingredient which has to be taken into account.

The highest T_c of 10.4 K ever obtained for an organic conductor has been reported in $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$ at ambient pressure [23]. Most of the features observed in this material are remarkably similar to those of the $(\beta\text{-H})\text{-I}_3$ salt. For instance, a field dependent peak of relaxation near T_c would indicate a common origin for superconductivity. It would be of great interest to pursue the characterization of this huge enhancement and decide on the existence of a possible magnetic contribution.

4. Conclusion

In this short review, we have presented some of the basic differences observed in physical properties of the $(\text{TMTSF})_2\text{X}$ and $(\text{BEDT-TTF})_2\text{X}$ families of organic superconductors. For the Bechgaard salt series and their sulphur analog, NMR experiments demonstrate that the pronounced quasi-1D character of these materials is at the origin of their magnetic

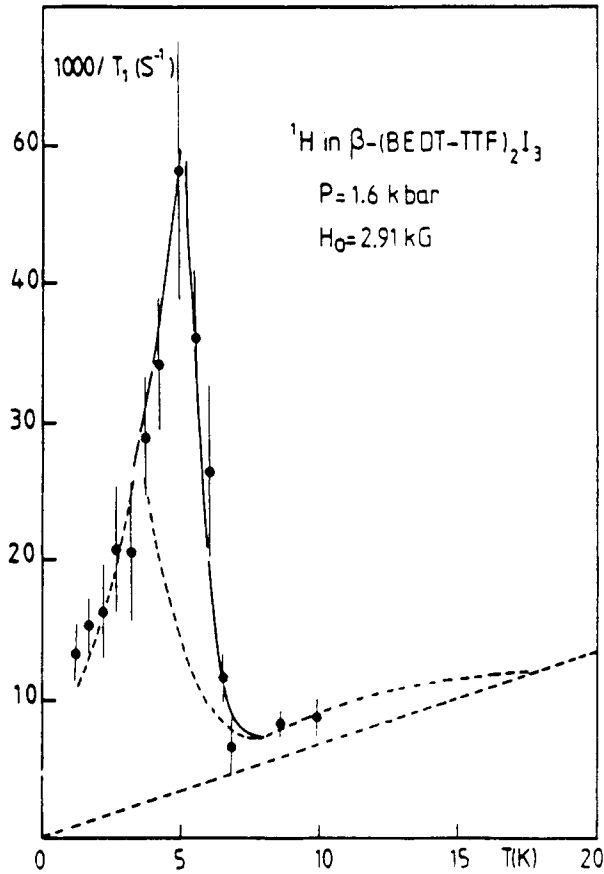


Fig. 6. ^1H powder spin lattice relaxation rate in $\beta\text{-}(\text{BEDT-TTF})_2\text{I}_3$ under 1.6 kbar at 2.91 kG. The dashed line represents the 6.08 kG data. After Ref. [22].

properties. Furthermore, the observed close proximity between antiferromagnetism and an apparent unconventional type of superconductivity supports the idea of a participation of spin fluctuations to a non-phonon mediated pairing mechanism. With a quasi-2D type of anisotropy, $(\text{BEDT-TTF})_2\text{X}$ contrast with the Bechgaard salts especially by showing a much higher superconducting T_c . Although there is a firm experimental evidence for an anomalous nuclear relaxation near T_c , the role of magnetism for superconductivity in these materials is less clear. Moreover, additional work is also needed to clarify the importance of quasi-two dimensionality in raising T_c .

References

1. For recent results in the field of organic conductors see: (a) Proceeding of the International Conference on Science and Technology of Synthetic Metals (ICSM'88), Santa Fe, NM, USA, June-July, 1988, Synthetic

- Metals, 27-29; (b) Proceedings of a NATO Advanced Study Institute on Low-Dimensional Conductors and Superconductors (Edited by D. Jerome and L. G. Caron), Vol. 155, Plenum Press, New York (1987).
2. Jerome, D. and Schulz, H. J., *Adv. Phys.* **31**, 299 (1982).
3. Bourbonnais, C., Proc. of the Enrico Fermi School on "Recent Trends in Condensed Matter Physics", Lerici, Italy, June 1988. To be published in Fermi School Series of North-Holland.
4. Moriya, T., *J. Phys. Soc. of Japan* **18**, 516 (1963).
5. Bourbonnais, C., Wzietek, P., Creuzet, F., Jerome, D. and Batail, P. and Bechgaard, K., *Phys. Rev. Lett.* **62**, 1532 (1989).
6. (a) Creuzet, F., Bourbonnais, C., Caron, L. G., Jerome, D. and Moradpour, A., *Synthetic Metals* **19**, 277 (1987). (b) Bourbonnais, C., Creuzet, F., Jerome, D., Bechgaard, K. and Moradpour, A., *J. Phys. Lett.* **45**, L755 (1984).
7. Miljak, M. and Cooper, J. R., *Mol. Cryst. Liq. Cryst.* **119**, 141 (1985); Miljak, M., Cooper, J. R. and Bechgaard, K., *J. Physique (Colloque)* **44**, C3-893 (1983).
8. Alloul, H. and Mihaly, L., *Phys. Rev. Lett.* **48**, 1420 (1982); Yoshimura, Y., Meketa, M., Takigawa, M., Takahashi, Y. and Yasuoka, H., *Phys. Rev.* **B37**, 3593 (1988).
9. Creuzet, F., Bourbonnais, C., Caron, L. G., Jerome, D. and Bechgaard, K., *Synthetic Metals* **19**, 289 (1987).
10. Coulon, C., Delhaes, P., Flandrois, S., Lagnier, R., Bonjour, E. and Fabre, J. M., *J. Physique* **43**, 1059 (1982).
11. Bourbonnais, C., Wzietek, P., Jerome, D., Creuzet, F., Valade, L. and Cassoux, P., *Europhys. Lett.* **6**, 177 (1988).
12. Bourbonnais, C. and Caron, L. G., *Europhys. Lett.* **5**, 209 (1988); *ibid.*, *Physica* **143B**, 451 (1986); Caron, L. G. and Bourbonnais, C., *Physica* **143B**, 453 (1986).
13. Gorkov, L. P. and Lebed, A. G., *J. Phys. Lett.* **45**, 2433 (1984); Heritier, M., Montambaux, G. and Lederer, P., *J. Phys. Lett.* **45**, L943 (1984).
14. Takigawa, M., Yasuoka, Y. and Saito, G., *J. Phys. Soc. Japan* **56**, 873 (1987); Hasegawa, Y. and Fukuyama, H., *J. Phys. Soc. Japan* **56**, 877 (1987).
15. Parkin, S. S. P., Engler, E. M., Schumaker, R. R., Lagier, R., Lee, V. Y., Voiron, J., Carneiro, K., Scott, J. C. and Greene, R. L., *J. Physique (Colloque)* **44**, G91 (1983).
16. Laukhin, V. N., Kostyvchewko, E. E., Sushko, Yu. V., Schegolev, I. F. and Yagubskii, E. B., *Sov. Phys. Jept. Lett.* **41**, 81 (1985); Murata, K., Tokumot, M., Anzai, H., Bando, H., Saito, G., Kajimura, K. and Ishiguro, T., *J. Phys. Soc. Japan* **54**, 1236 (1985).
17. Ravy, S., Pouget, J. P., Moret, R. and Lenoir, C., *Phys. Rev.* **B37**, 5113 (1988).
18. Creuzet, F., Creuzet, G., Jerome, D., Schweitzer, D. and Keller, H. J., *J. Phys. Lett.* **46**, L1079 (1985).
19. Murata, K., Toyota, N., Honda, Y., Sasaki, T., Tokumoto, M., Bando, H., Anzai, H., Muto, Y. and Ishiguro, T., *J. Phys. Soc. Japan* **57**, 1540 (1988).
20. Kubler, J., Weger, M. and Sommers, D. B., *Solid State Commun.* **62**, 801 (1987).
21. Jacobsen, C. S., *J. Phys. C: Solid State Phys.* **19**, 5643 (1986).
22. Creuzet, F., Bourbonnais, C., Jerome, D., Schweitzer, D. and Keller, H. J., *Europhys. Lett.* **1**, 487 (1986).
23. Urayama, H., Yamochi, H., Saito, G., Nozawa, K., Sugano, T., Kinoshita, M., Saito, S., Oshima, K., Kawamoto, A. and Tanaka, J., *Chem. Lett.* **55** (1988).
24. Takahashi, T., Tokiwa, T., Kanoda, K., Urayama, H., Yamochi, H. and Saito, G., *Synthetic Metals* **27A**, 319 (1988).