Unconventional Superconductivity in Layered Organic Superconductors

K. Lie
Department of Physics, 1110 West Green, Urbana, IL 61801-3080
(Dated 12/13/06)

Like the high-Tc copper oxides, organic superconductors are another class of superconductors that cannot be fully explained by the conventional BCS theory, due to the repulsive effective interactions between the charge carriers. Experiments display similarities between these systems and the high-Tc copper oxides in their pairing symmetry and their phase diagram. In this paper, some results from experiments in organics are summarized and a suggested model of this superconductivity induced by strong electron correlation is discussed.

I. Introduction: Challenge and Motivation

The discovery of the first high-temperature superconductor in 1986 has triggered a flurry of theoretical and experimental activities on high-Tc superconductivity. Since then there have been an increasing number of exotic materials with a variety of structures that are found to be high-Tc superconductors, with higher and higher Tc obtained (the highest record at author's time is 150K [1]). In spite of the rapid progress in "cooking up" new superconducting materials, there is little fundamental understanding of high Tc superconductivity. The BCS theory, while successfully provides a microscopic model for superconductors with critical temperature close to absolute zero (elements and simple alloys), is inadequate to explain the observed phenomena in high-Tc superconductors. A theoretical description of these type-II superconductors remains one of the greatest challenges in condensed matter physics over the past two decades [2].

Among the various high-Tc superconductors, the copper oxides (cuprates) are of the most widely studied. The unconventional properties in cuprates (layered or quasi-two-dimensional structure, high Tc, anisotropic pairing symmetry, small size of Cooper pair) suggest that the superconductivity in these materials is a non-BCS one.

Recently, a class of organic conductors based on BEDT-TTF ("ET") molecules has stimulated much interest due to their similarities with cuprates. These salts can have layered structure that leads to highly anisotropic electronic properties, which is a key feature of the cuprates [2]. There are also strong evidences that these organics exhibit unconventional symmetry in their pairing states as similar to that in cuprates [2]. Furthermore, the family of organic salts named κ -(BEDT-TTF)$_2$X (where BEDT-TTF is an organic molecule and X an inorganic anion) has a phase diagram that resembles the phase diagram of cuprates when pressure is replaced with doping [2].

In this paper I present a brief review of the studies in the organics. To maintain conciseness of the paper, I focus only on the nuclear magnetic resonance (NMR) in the experimental aspects. Results and implications from NMR studies on the mentioned ET salts are summarized. A model of superconductivity in two-dimensional organic

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

conductors based on the frustrated Hubbard model is discussed in address to theoretical progress and future direction of the field.

The goal of this paper is to give a survey of the subject to readers with minimal knowledge of the field but interested in knowing more about it. It is therefore intended to keep the technical and theoretical details at minimum and focus on the development of the field in a qualitative basis.

II. $(ET)_2X$ molecule – a quasi-two-dimensional organic superconductor

BEDT-TTF ("ET") is an electron-donor organic molecule. It can form charge-transfer salts (organic conductors) with various types of inorganic counter-anions. Among them, κ-$(BEDT\text{-}TTF)_2X$ is a family consists of conducting ET layers sandwiched between insulating anion (X) layers (the Greek letter κ preceding ET denotes a particular packing pattern of ET, which is a large planar molecule). These compounds have two-dimensional character in the electronic state due to their layered structure. In the κ-family, a dimer consists of two ET molecules stacked on top of each other forms the basic unit of the packing pattern. Upon binding with an anion, the dimer gives one electron to the anion therefore creating a hole. The hole can then hop from dimer to dimer within its layer and has a much less tendency to hop between layers. This consequently leads to a much higher conductivity parallel to layers than perpendicular to layers, and, therefore, highly anisotropic electronic properties in reminiscence of the high-Tc cuprates.

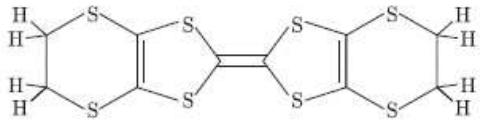

Figure 1. The bisethylenedithiotetrathiofulvalene (BEDT-TTF) molecule. Picture by Singleton *et al.* [3].

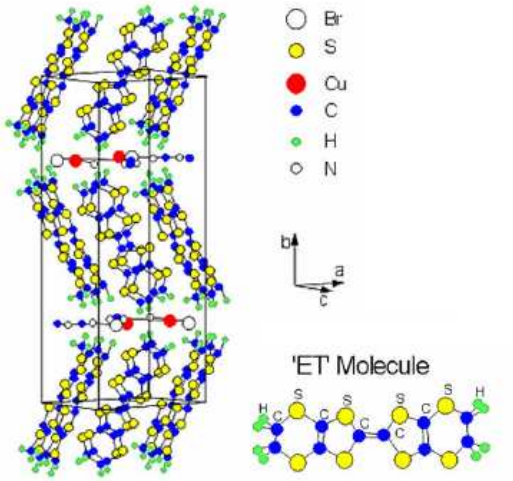

Figure 2. Molecular structure of κ-$(ET)_2Cu[N(CN)_2]Br$ [5]. The 'ET' dimers form conducting layers sandwiched between insulating layers of anions.

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

The family κ-$(ET)_2X$ exhibits an unconventional pairing symmetry and a particularly rich phase diagram (metallic, insulating, antiferromagnetic, superconducting) as a function of pressure, temperature and anion [2]. In the following section, we discuss experimental studies of pairing symmetry and electronic phases with NMR (nuclear magnetic resonance) (and briefly susceptibility measurements) on κ-$(ET)_2X$ salts of three different anions: X = $Cu(NCS)_2$, $Cu[N(CN)_2]Br$, and $Cu[N(CN)_2]Cl$.

Unconventional Pairing in Superconducting state

In BCS theory, the superconducting electron wavefunction (or order parameter), which arises from electron-phonon interaction, possesses isotropic or s-wave symmetry. This order parameter is proportional to the energy gap. Thus an s-wave pairing state corresponds to the presence of a uniform gap on the Fermi surface in all direction in **k**-space (absence of gap nodes). A superconductor that possesses s-wave (non-s-wave) pairing state thus is regarded as conventional (unconventional).

A variety of experiments have been conducted to probe the pairing symmetry of κ-$(ET)_2X$. Of all experimental techniques, NMR data of κ-$(ET)_2Cu[N(CN)_2]Br$ showed strong evidences that support an unconventional pairing state with possible nodes in the gap function [4][6][7]. De Soto *et al*. has shown a temperature dependence of the spin-lattice relaxation rate ($1/T_1$) at low temperature distinctive from a BCS behavior, which, they claimed, "rules out the possibility of an isotropic BCS s-wave energy gap" [4]. This observation had further confirmations from another group by Mayaffre *et al*. [6] and Kanoda *et al*. [7], both showing a T^3 dependence of $1/T_1$ at low T, therefore suggesting a very anisotropic gap [6][7] or possibly a *d*-wave pairing state [4][6]. In their data there was also no Hebel-Slichter coherence peak just below T_c being observed (its presence is a characteristic feature of s-wave BCS superconductors [4]), as shown in figure 3 [6]. These two evidences together suggest that the pairing state is an unconventional one and that the electron-phonon mechanism alone cannot be the source of the superconductivity.

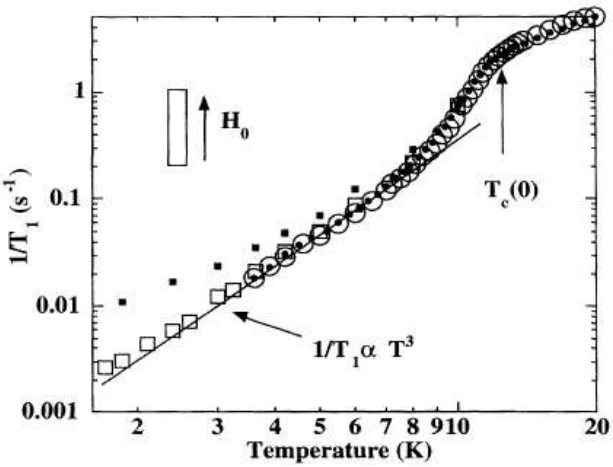

Figure 3. Data shown by Mayaffre *et al* [6]. $1/T_1 \propto T^3$ at low temperature. Spin-lattice relaxation rate decreases monotonically just below T_c, i.e. no Hebel-Slichter coherence peak.

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

Magnetism in κ-$(ET)_2X$

The magnetism of the normal state of the κ-$(ET)_2X$ family has been investigated with NMR by Kawamoto *et al.* (X = $Cu(NCS)_2$ and $Cu[N(CN)_2]Br$) and Miyagawa *et al.* (X = $Cu[N(CN)_2]Cl$). At ambient (i.e. surrounding) pressure, κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_2Cu[N(CN)_2]Br$ undergo a transition to their superconducting ground states at lower temperatures, while κ-$(ET)_2$ $Cu[N(CN)_2]Cl$, an insulator, does not undergo superconducting transition but a magnetic transition to antiferromagnetic ground state at lower temperature. Nevertheless, all of these materials exhibit strong antiferromagnetic spin fluctuations. In their experiments, the relaxation rate divided by temperature, $(T_1{}^0T)^{-1}$, was measured as a function of temperature. From an extended version of the Korringa relation to the case of anisotropic hyperfine coupling, $(T_1{}^0T)^{-1}$ can be evaluated in the case of uncorrelated electrons [8]. The evaluation yields a value from 0.006 sec^{-1} K^{-1} to 0.017 sec^{-1} K^{-1} [8,9,10]. From figure 4 one can easily see that the experimental values are enhanced by one or half order of magnitude than the evaluated values [8,10]. The large enhancement and the anomalous temperature dependence of $(T_1{}^0T)^{-1}$ are therefore considered to attribute to antiferromagnetic spin fluctuations with finite q vector [8,10]. It is noted that at just above the superconducting transition, a large enhancement in $(T_1{}^0T)^{-1}$ remains, indicating a highly correlated nature of the superconducting phase [10]. This implication is also shown later in the phase diagram of κ-$(ET)_2$ $Cu[N(CN)_2]Cl$ by the proximity of superconducting phase to the antiferromagnetic insulating phase in figure 5.

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

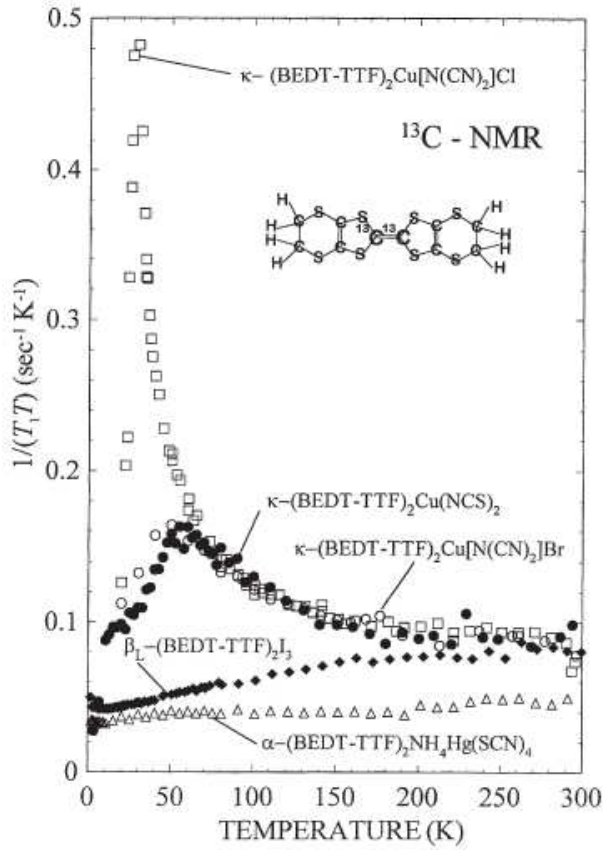

Figure 4. ^{13}C nuclear spin-lattice relaxation rate divided by temperature, $(T_1T)^{-1}$, for (BEDT-TTF)$_2$X. Data from Kanoda *et al*. [10].

Phase diagram

From the above experiments, researchers also found that by applying pressure (above 0.2 kbar) to κ-(ET)$_2$ Cu[N(CN)$_2$]Cl, the salt undergoes a superconducting transition at 13 K. This suggests the emergence of a pressure-driven superconducting phase situated in vicinity of an antiferromagnetic phase that possesses strong electron correlation [8], similar to the case in high-T_c cuprates when pressure is replaced by doping. On the other hand, Miyagawa *et al.* pointed out that the metal-insulator transition in the κ-type compounds is driven by electron correlation, i.e. a Mott transition, rather than disorder-induced localization [9]. This leads one to suggest the important role of strong electron correlations to superconductivity based on Mott transition. These facts suggest an exceptionally rich phase diagram most eminently manifested in the κ-(ET)$_2$ Cu[N(CN)$_2$]Cl salt. An accurate measurement to produce the phase diagram of κ-(ET)$_2$ Cu[N(CN)$_2$]Cl, showing a region where both SC and AF phases coexist, was done by Lefebvre *et al.* as shown in figure 5 [11].

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

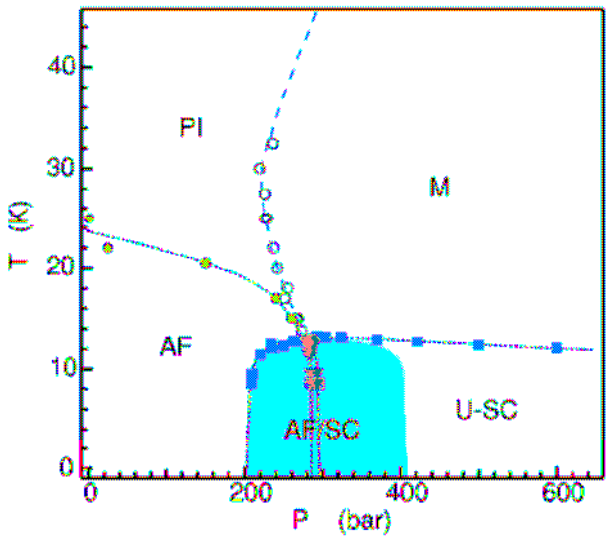

Figure 5. Temperature vs pressure phase diagram of κ-$(ET)_2Cu[N(CN)_2]Cl$. The antiferromagnetic (AF) critical line $T_N(P)$ (dark circles) was determined from NMR relaxation rate while $T_c(P)$ for unconventional superconductivity (U-SC: squares) and the metal-insulator $T_{MI}(P)$ (MI: open circles) lines were obtained from the ac susceptibility. The AF-SC boundary (double-dashed line) is determined from the inflection point of $\chi'(P)$ and, for 8.5 K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence (shaded area). Data from Lefebvre *et al.* [11].

III. Insights from recent experiments: Emergence of spin liquid from an organic Mott insulator

It is believed that the magnetism of the Mott insulator holds the key to understand the mechanism of the unconventional superconductivity, since it is the mother phase giving the superconductivity in the high-Tc cuprates and κ-$(ET)_2X$ organics [12]. The ground states of the Mott insulators we studied so far are antiferromagnets, a long-range magnetic order (LRMO) results from spontaneously broken symmetry. In a recent experiment, Shimizu *et al.* (2003) showed that the ground state with antiferromagnetism is not an absolute possibility: one can find insulating ground states with no long-range magnetic order! This is discovered in a unique class of κ-$(ET)_2X$ ($X = Cu_2(CN)_3$) that possesses a nearly isotropic triangular lattice. Their results showed no indication of LRMO down to 32mK [12].

Geometrical frustration

The system of the ET dimer pair can be effectively described by the Hubbard model on an anisotropic triangular lattice (figure 6) with a half-filled conduction band. The anisotropic triangular lattice of the interacting spins is described by the nearest neighbor transfer t and the second-nearest neighbor transfer t', as seen in figure 6. Its anisotropy gives rise to LRMO. However, if the lattice is nearly isotropic, i.e. $t'/t \sim 1$, then the geometrical frustration (a situation when there is no way to require the order of neighboring spins for the lowest energy state, since either orientations lead to the same

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

energy state: the spins are “frustrated”) works effectively against the LRMO. An exotic state without symmetry breaking, named a “spin liquid” can emerge [12].

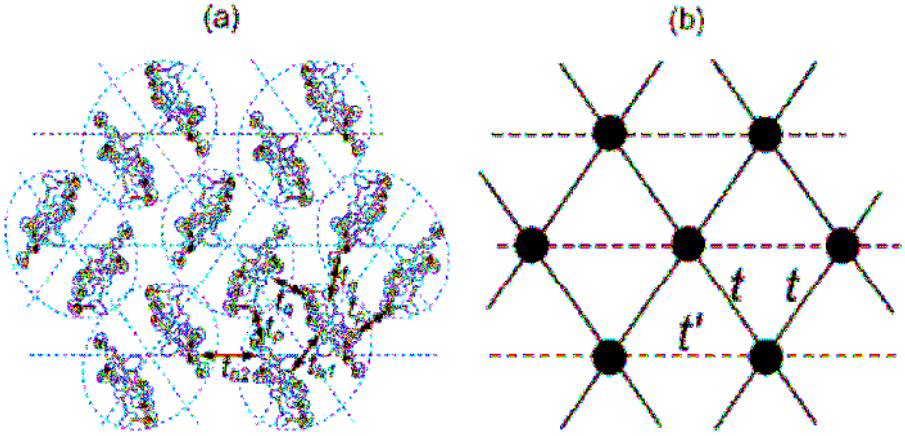

Figure 6. (a) Crystal structure of an ET layer of κ-$(ET)_2Cu_2(CN)_3$ viewed along the long axes of the face-to-face ET molecules [4]. t_{b1}, t_{b2}, t_p, and t_q are the transfer integrals between ET molecules. (b) Schematic representation of the electronic structure of κ-$(ET)_2X$, where the dots represent the ET dimer units. They form the anisotropic triangular lattice with $t = (|t_p| + |t_q|)/2$ and $t' = t_{b2}/2$. Picture from Shimizu *et al.* [12].

The ratio of transfer integrals in the Mott insulator κ-$(ET)_2Cu_2(CN)_3$ is almost unity ($t'/t = 1.06$), suggesting a nearly isotropic triangular lattice of this salt and that it is likely to be a spin liquid insulator [12]. This close-to-unity value of t'/t for κ-$(ET)_2Cu_2(CN)_3$ is unique among the κ-$(ET)_2X$ family.

Results of experiments

In the experiment, the result from ^1H NMR spectra indicated no LRMO exists in κ-$(ET)_2Cu_2(CN)_3$ at least down to 32mK, thus verifying the realization of the quantum spin liquid state due to strong spin frustration in a nearly isotropic triangular lattice [12]. The results contrasted sharply with another Mott insulator κ-$(ET)_2Cu[N(CN)_2]Cl$ with $t'/t \sim 0.75$, which undergoes the AF transition at $T_N = 27$ K at ambient pressure and SC transition at $T_C = 12.8$ K under pressure (figure 7) [12]. These results strongly suggest that the quantum spin liquid state is realized in the proximity of the superconducting phase under pressure [12]. To author’s knowledge, the emergence of superconducting and metallic phases from the spin liquid insulator has no analogues in high-T_C cuprates or other organic conductors, therefore is promised to reveal novel insights the our problem. A more recent study (2005) on this unique salt also confirmed the persistence of spin-liquid phase before the Mott transition to metallic or superconducting phase under pressure [13], with an empirical construction of the pressure-temperature phase diagram [13].

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

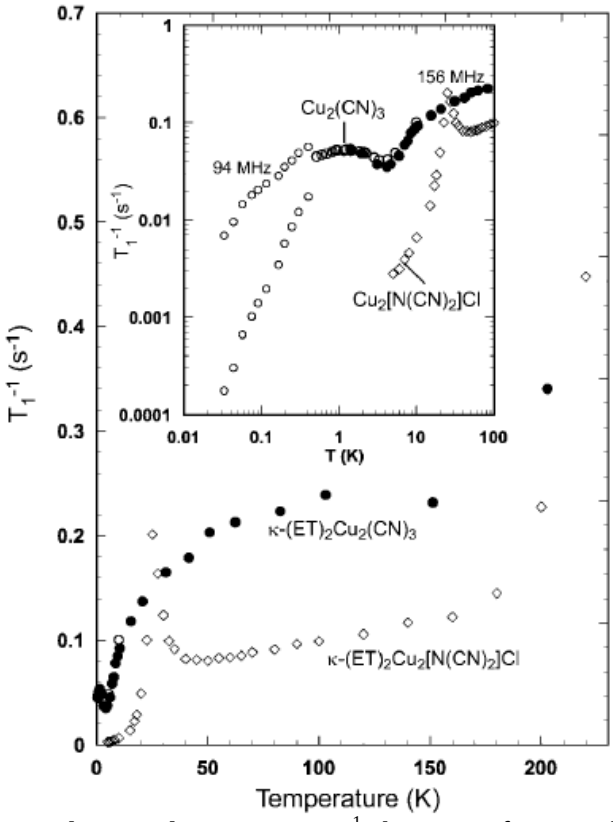

Figure 7. 1H nuclear spin-lattice relaxation rate T_1^{-1} above 1 K for a single crystal (open circles) and a polycrystalline sample (closed circles) of κ-$(ET)_2Cu_2(CN)_3$ and a single crystal of κ-$(ET)_2Cu[N(CN)_2]Cl$ (open diamonds) [9]. Data shown by Shimizu *et al*. [12].

IV. Remarks from theoretical calculations based on frustrated Hubbard model

Finally, I present corresponding results from theoretical calculations based on the frustrated Hubbard model in attempt to briefly address the theoretical progress in this field.

In response to the novel experimental results regarding the spin liquid state of κ-$(ET)_2Cu_2(CN)_3$ [12, 13], a very recent paper by Kyung *et al.* (2006), presented a phase diagram for layered organic conductors obtained by using cellular dynamical mean-field theory (CDMFT) for the frustrated Hubbard model [14]. In their calculations, all phases observed experimentally (*d*-wave superconducting (SC), metallic (M), antiferromagnetic (AF) and spin liquid (SL)) appeared in the phase diagram by considering physically relevant parameters for layered organic conductors (t'/t ; U/t, where U refers to Coulomb interactions between electrons). Their results showed that a *d*-wave SC phase appears between an AFI and a metal for t'/t = 0.3-0.7, or between a spin liquid and a metal for $t'/t \geq 0.8$, which are consistent with experiments. And for t'/t =1.0, close to the value of κ-$(ET)_2Cu_2(CN)_3$, a transition between a SL and SC is shown, in remarkable agreement with experiments by Shimizu *et al*. [12]. In light of these agreements with experiments,

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

they predicted a class of new materials with $t'/t \sim 0.8$-0.9 that would undergo a sequence of phase transitions from AFI to SL to *d*-wave SC to metal with increasing pressure [14]. Another prediction from their calculations was that the first-order transition between AF and SC phases, if the two phases are destroyed with an external magnetic field, should remain as a first-order Mott metal-insulator transition [14]. It is worthy to note that a previous experiment has shown evidence [15] to the second prediction by Kyung *et al.*.

V. Conclusion

In this paper, I reviewed various results and insights from experimental and theoretical studies on organic superconductors. According to experiments the organic κ-$(ET)_2X$ family exhibits very anisotropic pairing symmetry, and is likely to possess unconventional superconductivity. The magnetism and the phase diagram of κ-$(ET)_2X$ are discussed. Insights from recent experiments have shown the possibility of a new phase (spin liquid) at proximity to the superconducting phase, other than an antiferromagnet. The predictions from the theoretical calculation consistent with experiments have provided directions for further experimental tests of the model. It is generally believed that the unconventional superconductivity arises from strongly correlated electronic systems, and that the study of the transitions across antiferromagnetic phase (and spin liquid) and superconducting phase can reveal fascinating insights. The source of the unconventional superconductivity in layered structures like the high-T_C copper-oxides and the organic κ-$(ET)_2X$ family still awaits future experiments and theoretical studies to reveal.

[1] Superconductors.org
[2] R. H. McKenzie, Science, vol. **278**, 820 (1997)
[3] J. Singleton and Ch. Mielke, Contemp. Phys. **43**, 63 (2002).
[4] S.M. de Soto, C.P. Slichter, A.M. Kini, H.H. Wang, U. Geiser and J.M. Williams, Phys. Rev. B **52**, 10364 (1995);
[5] R. Prozorov, R. W. Giannetta, Supercond. Sci. Technol. **19** (2006) R1–R27
[6] H. Mayaffre, P. Wzietek, D. J´erome, C. Lenoir and P. Batail, Phys. Rev. Lett. **75**, 4122 (1995).
[7] K. Kanoda, K. Miyagawa, A. Kawamoto and Y. Nakazawa, Phys. Rev. B **54**, 76 (1996).
[8] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995)

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com

[9] K. Miyagawa, K. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995)
[10] H. Kanoda, Physica C **282**, 299 (1997); Hyperf. Int., 104, 235 (1997).
[11] S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérome, C. Mézière, M. Fourmigué, and P. Batail, Phys. Rev. Lett. **85**, 5420–5423 (2000)
[12] Y. Shimizu et al., Phys. Rev. Lett. **91**, 107001 (2003).
[13] Y. Kurosaki, Y. Shimizu, K. Miyagawa, K. Kanoda, and G. Saito, Phys. Rev. Lett. **95**, 177001 (2005)
[14] B. Kyung and A.-M. S. Tremblay, Phys. Rev. Lett. **97**, 046402 (2006)
[15] F. Kagawa, T. Itou, K. Miyagawa, and K. Kanoda, Phys. Rev. Lett. **93**, 127001 (2004)

This PDF was created using the Sonic PDF Creator.
To remove this watermark, please license this product at www.investintech.com