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Dynamic Phenomena in Superconducting Inorganic/Organic Metals

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Abstract

Dynamic electron spin resonance, ESR, and extended x-ray absorption edge fine structure, EXAFS, measurements suggest that all layer superconducting metals behave similarly, e.g., organic metals and cuprates. The response to microwave radiation in a modulated external magnetic field indicates that: (i) triplet state, T^* ESR is observed below T_c for all; (ii) the condensation of free spin doublet D (in organic metals) to T^* occurs above the transition temperature to superconductivity T_c (10 ± 1 K for the organic metal and 92 K to 12 K for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and its rare earth derivatives; (iii) there is antiferromagnetic (AF) resonance above T_c for the organic metal. Here the exchange field between the aligned AF domains $J_{\text{AF}}(150 \text{ K}) = 130.7 \text{ mT}$ (153 mK) is greater than the exchange term $J(150 \text{ K}) \approx 15 \text{ mT}$ (20 mK) between free spins, $S=1/2$, leading to T^* states; the lifetime of AF domains τ_{AF} decreases below 150 K and it is not detected below 44 K ($\tau_{\text{AF}} < 10^{-10} \text{ s}$) thus allowing a superconducting transition to occur below 10 K; (iv) the relaxation time τ_1 for the half field, triplet state ESR absorption increases fourfold near 10 K for the organic metal and, (v) the onset of superconductivity is detected in all superconductors by the appearance of an energy loss at exactly $H=0$ and, magnetization oscillations observed versus H below T_c when the samples are cooled in a non-zero field H . The spin-lattice relaxation time for the triplet state half field ESR near 10 K is interpreted using the Gorter phenomenological relation $\tau_1 = C_H/\alpha_H$, C_H and α_H are respectively the heat capacity and the thermal contact coefficient to the bath of the spin system, at constant field H . Complimentary changes in EXAFS edge intensity near T_c are correlated to electron-phonon interactions.

Introduction:

The most accurate methods used to determine the transition temperature T_c to the superconducting state (in addition to transport measurements) are based on the thermodynamics of the phase transition, i.e., the jump in the heat capacity, and others that are directly associated with this thermodynamic property such as the nuclear magnetic resonance, NMR, spin-lattice relaxation time of nuclei in hyperfine contact with the Bose condensate.¹ The value of T_c can also be ascertained by the appearance of an energy loss at exactly zero field.^{2,3} In this work, the transition to superconductivity of cuprates and a paramagnetic organic metal ($\text{BEDT-TTF})_x\text{Ta}_2\text{F}_{11}$,⁴ is ascertained from the onset of the energy loss at $H=0$ and magnetization jumps observed when the samples are cooled below T_c in $H \neq 0$. The triplet state ESR relaxation time τ_1 is related to the thermodynamic parameters by the Gorter,⁵ relation:

$$\tau_1 = C_H/\alpha_H \quad (1)$$

C_H and α_H are respectively the heat capacity and the thermal contact coefficient to the bath of the spin system, at constant field H . The spin system temperature T_s approaches the lattice temperature T_0 as:

$$dT_s/dt = (T_0 - T_s)/\tau_1, \text{ when } |T_0 - T_s|/T_0 \ll 1. \quad (2)$$

A common structural property of these metals is that they grow in separate donor/acceptor layers^{1,4}

The organic free radical cations ($S=1/2$) are aligned to maximize the chalcogen, π - π intermolecular interactions (figure 1). ESR measurements give information on the chemical dynamics that the paramagnetic free spin species undergo as a function of temperature.^{2,4} These charged free spin species interact with the lattice vibrations to produce a polarization, called a polaron.⁶ Alexandrov and Mott⁶ have shown that such charged carriers with spin $S=1/2$ in a many-electron system, strongly coupled to the lattice vibrations, can tunnel to form a charged Bose-liquid of small bipolarons with charge $2e$ and $S=0$ or 1 . This work applies the Alexandrov and Mott theory in order to understand the relation between the formation of the triplet state condensate and the superconductivity; the Gorter relation (1) is applied to the half field triplet state, T^* ESR lattice relaxation times for the organic metal near T_c . Thus τ_1 measurements for the T^* ESR may be able to ascertain whether the triplet state of the condensate is directly involved in the transition to superconductivity.

The complimentary EXAFS measurements probe the changes in L2,3 x-ray edge absorption for cuprates near T_c .

Experimental:

Single crystals: $(\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11}$ (from IBM)^{4b} and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (from the Cavendish)⁷ and, ceramics $\text{Nd}(\text{Ba}_{0.95}\text{Nd}_{0.05})_2\text{Cu}_3\text{O}_{7-\delta}$ (from Morris Laboratories)² and $\text{Pr}(\text{Ba}_{0.975}\text{Pr}_{0.025})_2\text{Cu}_3\text{O}_{7-\delta}$ (from Notre Dame U.)⁸ were measured at SJSU with an x-band Bruker-ER300/Oxford-900 spectrometer /cryogenic system,^{2,4} and at SSRL, as described earlier for TaS_2 .⁹ Figures 1 to 4 show the power absorption derivative dP/dB_z response to the field $k(B_z + 2B_m \cos(2\pi\nu_m)) + 2iB_1 \cos(2\pi\nu)$ with $\nu = 9.36$ GHz, $\nu_m = 10^5$ Hz, $B_1 = B_{10} E - dB/20$, $B_{10} \leq 0.1$ mT, versus B_z and temperature T from 280 K down to 3.7 K when $B_1 \parallel a \perp B_z$: near zero field (energy loss in the superconducting state exactly at $H = 0$ ^{2,3}) ESR near $g = 2.00$ (D and T^* , $\Delta S_z = \pm 1$) and, near the half field resonance (T^* , $\Delta S = 0$), antiferromagnetic AF resonance,² and magnetization oscillations,¹⁰ when $T < T_c$ if the sample is cooled in $H \neq 0$. Figures 5 and 6 show the Nd L3 x-ray and Ba L2 x-ray edge data versus T for $\text{Nd}(\text{Ba}_{0.95}\text{Nd}_{0.05})_2\text{Cu}_3\text{O}_{7-\delta}$ and for $\text{Pr}(\text{Ba}_{0.975}\text{Pr}_{0.025})_2\text{Cu}_3\text{O}_{7-\delta}$ respectively.

Discussion of Results:

Four types of magnetic response are identified in figures 1 to 6 by their orientation dependence in the external magnetic field as described in the literature.^{4,5} For the organic metal (figure 1) these are: (i) ESR of D and T^* states versus temperature and microwave power; (ii) AF resonance which identifies the direction and magnitude of the anisotropy field $\pm B_A(220 \text{ mT}) \parallel b$ -axis in the AF domains and the field produced by exchange interactions $B_E = 130.7 \text{ mT}$. (iii) The onset of the energy loss at exactly $H=0$ identifies T_c ,^{2,3} by the appearance of a signal of opposite polarity to the ESR near T_c , (iv) Another signature of superconductivity observed is the appearance of magnetization jumps (due to flux pinning) when samples are cooled in $H \neq 0$ through T_c (figures 1, 2 and 3),¹⁰ they disappear when the samples are cooled through T_c in zero field.

The sharp ESR absorptions found in organic conductors allow the measurement of spin relaxation times vs T (figure 1b); a fourfold increase in τ_1 , which occurs near the same temperature as the onset of an energy loss signal at $H=0$ and, magnetization oscillations when the crystal is cooled in $H \neq 0$, may be used to relate it to T_c using the Gorter

phenomenological relation (1) and, to the rate processes between the states in figure 7. There are five spin states split by the field ($B_z \approx 156 \text{ mT}$) in dynamic equilibrium; the ground state is a singlet S in equilibrium with the D states and the latter are in equilibrium with the T^* states via the chemical reactions:

with equilibrium constants:

$$K_2 = (a[D])^2/a[S] = \exp(-\Delta_{S,D}/2T),$$

$$K_3 = k_1/k_{-1} = a[T^*]/(a[D])^2 = \exp(\Delta_{T^*,D}/2T). \quad (4)$$

The $a[i]$ are ascertained from D, T^* $\Delta S_z = \pm 1$ ESR intensity measurements, in the absence of saturation above T_c , when $a[S] \cong 1$; relation (4) obtains the temperature dependence of the band gaps: $\Delta_{S,D}/2$ and $\Delta_{T^*,D}/2$ (insert figure 7). The rate constant k_1 is determined from the line width of the D $\Delta S_z = \pm 1$ ESR vs $1/T$ (figure 1b):

$$\Delta B_{z,ms} = \text{constant}(k_1 + 1/T_2),$$

$$k_1 = A_0 e^{\Delta S/R} e^{-\Delta U/RT}, \quad (5)$$

where $(\Delta U/R, A_0 e^{\Delta S/R}) = (111 \text{ K}, 3.5 \cdot 10^7/\text{s})_{T > 150 \text{ K}}$; $(11 \text{ K}, 7 \cdot 10^6/\text{s})_{T < 150 \text{ K}}$; ΔU and ΔS are respectively the activation energy and entropy to form the activated states leading to the disappearance of D.

The decrease in ΔU below 150 K indicates that there is an easier path for the disappearance of D whereas the entropy increase, by $\approx 2R$ above it, suggests that disorder is introduced when the T^* states do not provide a reaction path (e.g., by the two possible spin flips, for each of the three singlet states formed by antiparallel pairing, along each of the principal axes of triplet state formation X_T, Y_T, Z_T , in figure 1a, each contributing $R \ln 2$ to the entropy). Tunneling of D polarons via lattice vibrations pair the spins to generate S^* states with $1/4$ probability and, T^* states with $3/4$ probability; the S^* states relax to the ground state S but the transition $T^* \rightarrow S$ is forbidden.

All the dynamic phenomena, the population and rates of disappearance and formation of the D, S^* and T^* states depend on the coupling of spins to the lattice vibrations. The spin system S (with components separated in energy by ΔE) obey a Boltzmann population distribution, i.e., $n_{S,Sz}/n_{S,-Sz} = \exp(-\Delta E/k_B T_s)$, where in a saturation experiment the spin temperature T_s is greater than the bath temperature T_0 and thermal equilibrium is obtained as the Boltzmann temperature approaches T_0 according to relation (2).

FIG 1: $(\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11}$ ($a=1.6683$, $b=1.1928$, $c=1.255\text{nm}$) $B_z \perp B_1 \parallel a$ -axis, $\theta = b^*B_z$, dP/dB_z vs B_z response to the applied fields: (a) Resonance fields; energy loss and magnetization oscillations near 3.7 K (for sample cooled through T_c in non-zero field due to flux pinning with periods of 10^0 mT near $B_z \approx 10^2$ mT to 100 mT near $B_z \approx 1$ tesla) these disappear when the sample is cooled in zero field through T_c ; T dependence of low field AF resonance and appearance of T^* , $\Delta S=0$ ESR absorption below 150 K..

(b) Temperature dependence of the doublet D ESR absorption line width between the points of maximum slope $\Delta B_{z,ms}$; Orientation dependence of AF $B_{z,AF}$ vs θ . fitted to the theory for $B_A=1.7 B_B = 220$ mT (solid line) and τ_1 vs T for $T^* \Delta S=0$ transition measured by saturation experiments.

FIG. 2: ESR $\text{YBa}_2\text{Cu}_3\text{O}_{7.3}$ 5K, Single crystal $T^* \Delta S=0$ signal is weak near T_c (cooled in $H=0$ and in $H \neq 0$).

FIG. 3: $\text{Nd}(\text{Ba}_{0.95}\text{Nd}_{0.05})_2\text{Cu}_3\text{O}_{7-\delta}$ ESR at 298 K: An impurity is superposed on the sample ESR near $g = 2$ as indicated by the sharp reference marker. Saturation of the sample requires that the spectra be measured at very low microwave powers. At 20 dB attenuation the extra amplitude at low fields indicates that $^{145,143}\text{Nd} (I = 7/2, 12.2 \text{ and } 8.3\% \text{ abundant})$ hyperfine components are broadened by the microwave power. At 70 dB the hyperfine components for the two isotopes $^{145}\mu, ^{143}\mu = 1.57$ are identified, in the wings, where there is no impurity ESR, by the relative intensities and coupling constant $^{145}A = 1.5, ^{143}A = 6.5 \text{ mT}$. Near T_c (72 K) the ESR absorption is broadened and vanishes. Very broad $T^* \Delta S = 0$ resonance may be present near 3.7 K, but this is not as strong as for the Pr substituted ceramic in figure 4.

FIG. 4: $\text{Pr}(\text{Ba}_{0.975}\text{Pr}_{0.025})_2\text{Cu}_3\text{O}_{7-\delta}$ ESR vs T. At room temperature the $g=2$ ESR absorption is due to an impurity but, at 3.4 K the sample resonance appears much stronger than that for the impurity. The temperature development of the ESR absorption indicates that the broad signal observed at 23 K narrows by 19.5 K, suggesting that a phase transition has occurred between these temperatures. As the temperature is decreased $T^* \Delta S = 0$ ESR appears. The high field absorptions may be related to Pr^{2+} and Pr^{4+} ESR, Pr^{3+} is a non Kramers ion.

Do you show the result?

(b) Radial amplitude at 147 ± 3 K

Radial amplitude at 80 ± 10 K

Radial amplitude at 6.4 K

FIG. 5: $\text{Nd}(\text{Ba}_{0.95}\text{Nd}_{0.05})_2\text{Cu}_3\text{O}_{7-\delta}$ Nd L3 x-Ray edge absorption spectra (a) EXAFS vs T taken at SSRL. Neither the pre-edge nor the edge white peak due to,⁹

$2p_{3/2} \rightarrow \text{nd}$ conduction band states

transitions change as the temperature is ramped through T_c . However the postedge (EXAFS region) becomes more transparent only near T_c . (b) radial distribution functions obtained from the analysis for different T (compared to 0K structure curve fit $\cdots$). These indicate that the photoelectric effect is enhanced at the transition to superconductivity.

FIG. 6: $\text{Pr}(\text{Ba}_{0.975}\text{Pr}_{0.025})_2\text{Cu}_3\text{O}_{7-\delta}$ Ba L2 x-Ray edge absorption spectra EXAFS vs T taken at SSRL. The temperature dependence of the white peak, due to:

$2p_{1/2} \rightarrow \text{nd}$ conduction states

transitions indicates that the population of the conduction band increases as T decreases.

The x-ray data in (figures 5, 6) indicate that the conduction band in the ceramic has d-character. Cu Kedge measurements by us as well as other groups show little change in the EXAFS vs T.

X-ray and EXAFS measurements are complementary to the ESR results in that the presence of single phase materials can only be ascertained by diffraction. Also, diffraction measurements appear to give tetragonal symmetry when the orthorhombic crystals are highly twinned (e.g., the Nd ceramic in figure 3). However, the most important observation here is that while the D ESR is sharp for the organic metal single crystal, the D ESR ($g=2$) in cuprates may be due to an impurity phase and/or, to oxygen free radicals formed in a,b twinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ orthorhombic structures (figure 2); the D ESR is not present in good single crystals (figure 2, $T_c = 85$ K) but, the $T^* \Delta S=0$ ESR is observed at sample level concentration in all cuprates investigated below T_c , suggesting that indeed these states are involved in the transition to superconductivity and the formation of bipolarons; The presence of D ESR may not be due to impurity states in twinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ orthorhombic structures. Figure 2 shows the absence of D ESR in a good single crystal, however both D and T^* ESR are observed in other highly twinned single crystals. This suggests that in mosaic a,b twins where there are breaks in the O-Cu-O chains, mobile oxygen free radicals (as proposed by Dow and Blackstead,¹¹) may give rise to detectable $g=2$ D ESR.

The hyperfine contact with neighboring atoms allows the identification of the site involved.² The hfs structure in figure 3 is detected for the $g=2.13$ absorption at low B_1 fields (70 dB). The root mean square relaxation time for the hyperfine lines at room temperature is estimated to be $\sqrt{\tau_1\tau_2} = 40$ μs (two orders of magnitude greater than for the organic metal). Two isotopes of $^{145,143}\text{Nd}$ both with $I=7/2$ and natural abundance of 12.2 and 8.3 %, respectively, give rise each to eight line hyperfine components with coupling constants in the same ratio of the respective nuclear moments, i.e., $^{145}\text{A}/^{143}\text{A} = \mu^{145}/\mu^{143} = 1.57$ is confirmed in figure 3 from the ESR in the wings, the highest intensity corresponds to the most abundant isotope, i.e., $^{145}\text{A} = 6.5$ mT. The whole $g=2$ ESR (figure 3) broadens and disappears below T_c , indicating that the absorber is isolated by the Meissner effect. The different rates of saturation for the three lines show that the $g = 2.06$ and 2.2 saturate much more slowly than the $g=2.13$ hfs. The relative intensities, however are at sample concentration and the two may be related, i.e., the $\text{Nd}^{3+} (^4\text{I}_{9/2})$, already observed in dilute ethylsulfates with $g=2.16$ and 3.65 , most probably gives rise to the hfs at $g=2.14$ whereas the $g=2.06$

and 2.2 lines with undetected hfs may arise from oxygen free radicals/ Cu^{2+} formed on twinning.

The room temperature $g=2$ ESR from the Pr ceramic (figure 4) appears to be due to an impurity because its relative intensity remains insensitive to any phase transition that the ceramic undergoes with temperature. The important observation in figure 4 however is that below 23 K a sample strength ESR appears. The line shape changes below 20 K indicate that a phase transition has occurred near that temperature and the flux expulsion observed below 19 K suggest that superconductivity is present. The $T^* \Delta S=0$ transition at half field is easily identified. However, higher field ESR absorptions growing at different rates suggest that Pr^{2+} and/or Pr^{4+} are present, $\text{Pr}^{3+} (^3\text{H}_4)$ is a non-Kramers ion and is not expected to give an ESR absorption. $\text{Pr}^{2+} (^4\text{I}_{9/2})$ ESR has been observed in CaF_2 ,⁵ and when Pr substitutes in the Ba layer of the ceramic, its valence may be forced to be +2 just as in CaF_2 . The ESR lines that grow the most as T decreases to 6.5 K ($g=3.5$ and 1.5) are assigned to $\text{Pr}^{2+} (^4\text{I}_{9/2})$ by comparison with the literature,⁵ this is evidence for more than 5% Pr substitution in the Ba layer.

The EXAFS (figures 5 and 6) give little evidence for multiple valence in the Nd L3 edge, however, the important observation is that the radial amplitudes increase near T_c . The experimental EXAFS radial amplitudes (solid lines figures 5 b) are compared with the 0 K ideal structure (-.-): near 150 K, near T_c and at 6.2 K. The radial amplitudes are weaker than the ideal at 150 K (due to lattice motion); they approach the ideal value as $T \rightarrow 4$ K but, they increase over the ideal value near T_c , suggesting that the onset of electron-phonon coupling near T_c enhances the photoelectric effect, which gives rise to the EXAFS. This needs to be investigated further.

The temperature dependence of the white peak near the Ba L2 x-ray edge (figure 6) suggests that the transition is similar to those found in TaS_2 :⁹

$\text{Ba } 2p_{1/2} \rightarrow \text{nd}$ conduction band states

is enhanced as T decreases. An edge shift observed below 20 K is being investigated, especially because both the ESR and Ba L2 edges indicate that the sample is undergoing a transition.

The value of doing complimentary EXAFS and ESR investigations lies in the fact that the latter can give information on the presence of paramagnetic states but the former also give information on changes of valence and phonon-scattering changes produced by fluctuations near T_c .

The ESR and EXAFS depend on the chemical rates, the spin-spin and spin-lattice, and spin-radiation interactions via the rates $w(\Delta E)$ between the states separated by ΔE in figure 7. It has been shown that the most efficient processes involve resonant phonons produced via second order Raman processes,⁵ by the absorption and emission of phonons, involving an intermediate state, at frequencies ν_1 and ν_2 when $\nu_2 - \nu_1 = \nu$:

$$E_{|S, S\rangle} + h\nu_{\text{radiation}} = E_{|S, S\rangle} \Rightarrow E_{|S, S\rangle} + h\nu_1 = E_{\text{intermediate}}; \\ \text{and } E_{\text{intermediate}} - h\nu_2 = E_{|S, S\rangle}. \quad (6)$$

The phonon temperature and heat capacity (T_{ph} , C_{ph}) depend on the contact with the lattice at temperature T_0 and infinite heat capacity and, the $w(\Delta E)$ depend on the energy transfer path:

Spin System(T_s , C_H) $\Rightarrow$ Resonant Phonons (T_{ph} , C_{ph}) $\Rightarrow$ Bath (T_0 , Infinite Heat Capacity),

$C_{ph} < C_H$ indicates that there may be a bottleneck when phonons are involved in phase transitions. The magnetization relations for the processes in figure 7 obtain:⁴

$$1/\tau_1(h\nu) = w^-(h\nu) + w^+(h\nu) + (w^-(h\nu/2) + w^+(h\nu/2))/2 + k_1. \quad (7)$$

and the fourfold τ_1 increase near 10 K for the organic metal suggests that a phonon bottleneck has decreased the rates $w(\Delta E)$ and that the lifetime of T^* is determined by $1/k_1$, which also depends on the lattice vibrations. In order to associate T_c with the τ_1 increase, the Gorter relation (1) obtains:
 $\Delta(\tau_1, T_c)/\tau_1 = \Delta C_H/C_H - \Delta\alpha_H/\alpha_H \approx 4. \quad (8)$

The EXAFS measurements versus T indicate that near T_c , fluctuations reduce the phonon incoherent scattering but increase the coherent interactions in cuprates is an effect similar to (8) (figure 5b). This must be compared with heat capacity C_p and thermal conduction coefficients K near T_c (C_H and α are the electronic contributions of the spin system to the latter); C_p and K are known accurately for cuprate superconductors; $\Delta C_p(T_c)/C_p \approx 0.03$, $\Delta K(T < T_c)/K = 0.3$,¹ for $YBa_2Cu_3O_{7.8}$ but many authors,¹ estimate that the electronic contributions are $\Delta C_e(T_c)/C_e \approx \Delta K_e(T < T_c)/K_e \geq 3$ to 4. If the latter applies also to organic superconductors, an increase in α below T_c would lead to the τ_1 decrease in figure 1b. Similarities between the organic and the cuprate superconductors is obtained from the T^* half field ESR absorption by a single crystal $YBa_2Cu_3O_{7.8}$

($T_c = 85$ K)⁸ and ceramics as well observed only below T_c (figure 2, 4, cooled in $H = 0$ and in $H \neq 0$). The absence of D ESR below T_c suggests that k_1 is shorter than 10^{-10} s, i.e. ΔU in (5) is lower for the latter. If ΔU for tunneling in the organic conductor varies inversely proportional to the corresponding S-S bond order (10^{-3}) and if the lifetime of the doublet state in cuprate superconductors is determined by O-O polarization interactions in the CuO_2 plane (with a the bond order 10^{-2} between sigma bonded O-O pairs at $\langle r_{OO} \rangle \approx 0.27$ nm)¹² ΔU is an order of magnitude smaller for the latter. Competition between AF and superconductivity in the organic metals is similar to that found in superconducting oxides.² The exchange fields near 150 K, $J_{AF} = 130$ mT $> J \approx 15$ mT suggest that at these temperatures superconductivity is not allowed by the presence of AF domains in the single crystal, however as the lifetime τ_{AF} of the latter decreases below 10^{-10} s (indicated by the increase in the AF resonance line widths) may be a reason why the superconducting transition is allowed near 10 K. The decrease in the bipolaron binding energy (figure 7) with T suggests that it may continue to decrease as $T \rightarrow J \approx 20$ mK; then if the T^* gap states contribute to the transport and $1/2 \Delta_{SD} \rightarrow J$ as $T \rightarrow J$, the transport properties at high magnetic fields (which destroy superconductivity but, lower T^* states) will depend on T as is true in superconducting cuprates.¹³ The weak magnetic fields used in the measurement of τ_1 (150 mT) can not destroy the superconductivity.¹

Conclusions:

The change in the D, ESR line shape and the appearance of the T^* , $\Delta S = 0$ ESR identifies the transition temperature where the pairing of doublet polaron states produce a triplet condensate in the organic metal near 150 ± 10 K but AF domains are also present at these temperatures in the organic metals. This is of some importance for any theory of superconductivity which predicts the formation of a Bose condensate above $T_c = 10 \pm K$.^{5b} The fact that the $T^* \Delta S = 0$ ESR is present for all layer superconductors investigated below T_c suggests that these are part of the superconducting condensate, especially in the organic metal where the relaxation time increases fourfold near T_c .

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Figure 7: (BEDT-TTF)₃Ta₂F₁₁: Energy level diagram near B_{z,1/2}. The insert shows the free enthalpy, obtained from equilibrium constants (4).

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Fig 1

F162

F163

F165

(a)

(b)

F162

(BEDT-TTF)₃Ta₂F₁₁ Energy Level Diagram in B_{z,1/2}