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Dynamic phenomena in organic metal \((\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11}\)

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Dynamic phenomena in superconducting organic metals by ESR

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Abstract:

Dynamic electron spin resonance, ESR measurements suggest that \((\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11}\) a paramagnetic, layer, organic metal, has similar properties as cuprate superconductors. The response to microwave radiation in a modulated external magnetic field indicates: (i) there is a condensation of free spin doublet to triplet states below \(T_{00}=150\pm10\text{K}\); (ii) \(T_{00}\) is above the transition temperature to superconductivity \(T_c=10\pm1\text{K}\) (detected by the onset of an energy loss at exactly \(H=0\)) because (iii) antiferromagnetic AF resonance is observed down to 85 K; (iv) the relaxation time \(\tau_1\) for the half field, triplet state ESR absorption increases fourfold near 10 K and, (v) the onset of superconductivity is also detected by the appearance of magnetization oscillations below \(T_c\) when the sample is cooled in a non-zero filed \(H\). Near 150 K the exchange field between the aligned AF domains (ascertained from the AF resonance orientation field dependence) \(J_{AF}=130\text{ mT (10}^2\text{ mK)}\) is greater than the exchange term \(J\approx 15\text{ mT (13 mK)}\) between free spins, \(S=1/2\) (estimated from the \(g=2\) line shapes). The presence of AF domains below 150 K is assumed to be the reason why the superconducting transition is observed only below 10 K. The spin-lattice relaxation time for the triplet state half field ESR near 10 K is interpreted using the Gorter phenomenological relation \(\tau_1=C_{TH}/\alpha_{TH}\), \(C_{TH}\) and \(\alpha_{TH}\) are respectively the heat capacity and the thermal contact coefficient to the bath of the spin system, at constant field \(H\).

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Introduction:

Some of 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.\(^2,3\)

The transition to superconductivity of the paramagnetic organic metal $(\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11},$\(^4\) is ascertained in this work from the onset of the energy loss near $H=0$ and magnetization jumps observed when the samples are cooled below $T_c$ in $H \neq 0$ and, the relaxation time $\tau_1$ which is related to the thermodynamic parameters by the Gorter,\(^5\) relation:

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

where $C_H$ and $\alpha_H$ are respectively the heat capacity and the coefficient of thermal contact of the spin system (at temperature $T_S$) to the lattice (at temperature $T_0$) at constant field $H$ and, the spin temperature changes with time as:

$$dT_S/dt = (T_0-T_S)/\tau_1, \text{ when } |T_0-T_S|/T_0 << 1. \quad (2)$$

The paramagnetic layer organic metal $(\text{BEDT-TTF})_3\text{Ta}_2\text{F}_{11}$ (figure 1a) consists of anion acceptor layers $\text{Ta}_2\text{F}_{11}^-$ and of donor layers where the $((\text{CH}_2)_2\text{S}_2\text{C}_2\text{S}_2\text{C} = \text{CS}_2\text{C}_2\text{S}_2(\text{CH}_2)_2)_3^+$ free
radical cations \((S=1/2)\) are aligned 20° from the c-axis to maximize the chalcogen, \(\pi-\pi\) intermolecular interactions. ESR measurements have already given information on the chemical dynamics that the free radical undergoes as a function of temperature (figure 1b).\(^{4a}\) The change in the inverse temperature dependence of the line width \(\Delta B_{x,ms}\) for the \(g=2.00\) doublet \(D\), and the appearance of triplet state \(T^*\) indicate that new phenomena are present below the temperature \(T_{00} = 150\pm 10\)K. A transition below 7 K was ascertained earlier from the broadening of the \(D\) and \(T^*\) ESR near \(g=2\). A charged free spin species interacting with the lattice vibrations produces the polarization called a polaron.\(^{6}\) Mott, and Alaxandrov and Mott,\(^{6c}\) have shown that such charged carriers with spin \(S=1/2\) in a many-electron system, when they are strongly coupled to the lattice vibrations, can tunnel to form a charged Bose-liquid of small bipolarons with charge \(2e\) and \(S= 0 \) or \(1\). The purpose of this work is to apply the Alexandrov and Mott theory to \((BEDT-TTF)_2Ta_2F_{11}\), in order to understand the transition near \(T_{00}\) and, to ascertain the transition to superconductivity by applying the Gorter relation (1) to the half field \(T^*\) ESR lattice relaxation times, i.e., the Gorter phenomenological relation may be applied to the ESR of the carriers directly responsible for the transition to superconductivity in the same manner that the beautiful NMR work applied the BCS theory to cuprate superconductors using the relaxation times of fixed nuclei in hyperfine contact with the condensate.\(^{1b,c}\) In the thermodynamic, phenomenological description the important parameters in the transition to superconductivity are the jump in the heat capacity and, in the thermal contact coefficient near \(T_c\); thus \(\tau_1\) 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.
Experimental:

The 10 mg oriented single crystal of (BEDT-TTF)$_3$Ta$_2$F$_{11}$ (figure 1a) was prepared at IBM,$^{4b}$ the $x$-band Bruker-ER300/Oxford-900 spectrometer/cryogenic system used for the measurements was described earlier.$^{2,4a}$ Figures 2a-d show the power absorption derivative $\frac{dP}{dB_z}$ response to the field $k(B_z+2B_{zm}\cos(2\pi v_m))+2iB_1\cos(2\pi v)$ with $v=9.36$Ghz, $v_m=10^5$Hz, $B_1=B_{10}E_{dB}/20$, $B_{10}$=0.1mT, versus $B_z$ and temperature $T$ from 280 K down to 3.7 K when $B_1||a$, $B_z$=0: near zero field (energy loss in the superconducting state exactly at $H=0$,$^{2,3}$) ESR near $g$=2.00 (D and $T^*$, $\Delta S=\pm 1$) and, near the half field resonance ($T^*$, $\Delta S=0$), antiferromagnetic AF resonance,$^2$ and magnetization oscillations,$^7$ when $T<T_c$ if the sample is cooled in $H=0$. For comparison figure 3 shows the ESR of a 1 mg YBa$_2$Cu$_3$O$_{7-\delta}$ ($T_c$=85 K) prepared by C.T. Lin at the IRC for Superconductivity, Cambridge, UK.$^8$

Results and Discussion:

Four types of response (figure 2) are identified by their orientation dependence in the external magnetic field as described in the Appendix:$^{2,4,5b}$ (i) The ESR fields $B_{z1}$ (figure 2a) for doublet and triplet states depend on the photon energy $\hbar\nu$ and the crystal orientation in the external field. The important parameters for the discussion are the $g$ factors ($g_{xx},g_{yy},g_{zz}$)=(2.0125,2.0030,2.0023) obtained from relations (A1) for the D states as well as the temperature dependence of the line shapes reported earlier (figure 1b).$^4$ Figure 2d shows the reversible change in the D ESR line shape; near the center, the lines are as sharp as above $T_{00}$ but, the amplitude in the wings is greater below $T_{00}$. The Anderson and Weiss theory,$^{5b,c}$ is applied to explain the line shape below $T_{00}$ in the Appendix, and to obtain an exchange field
The $T^*$, $\Delta S=0$ transition saturates faster than the $D$, $\Delta S_z=\pm 1$ (figures 2a,c,d). The spin-lattice relaxation times (figure 4a) are measured by saturation experiments using relation (A4). (ii) AF resonance at fields $B_{z,i}$ (figure 2b) depend on the photon energy $h\nu$, the crystal orientation in the external field relative to the direction of the anisotropy field $B_A$ produced in the different AF domains. The important parameters obtained from the orientation dependence (figure 4b) using relation (A2) are the anisotropy field $B_A=220$ mT, and the field produced by the exchange interaction between spins in the different domains, $B_E=130$ mT, $J_{AF}=10^2$ mK and $g=1.74$, correct to 10% accuracy. (iii) The onset of the energy loss at exactly $H=0$ (figure 2a) identifies $T_c$, by the appearance of a signal of opposite polarity to the ESR near $T_c=10\pm 1$ K. (iv) Another signature of superconductivity observed is the appearance of magnetization jumps (due to flux pinning) when the crystal is cooled in $H\neq 0$ through $T_c$, these disappear when the sample is cooled through $T_c$ in exactly zero field (figure 2a). The onset of the latter two responses have been used in the literature to identify the transition to superconductivity at $T_c$ for metal superconductors. The sharp ESR absorptions (figure 2) now allow the measurement of spin relaxation times vs $T$.

The fourfold increase in $\tau_1$ (figure 4a) 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 $H\neq 0$; it may be used to relate $\tau_1$ to $T_c$ using the Gorter phenomenological relation (1) and the rate processes between the states in figure 5: There are five spin states split by the field ($B_{z,i}\approx 156$ mT) in dynamic equilibrium: two $D$ states ($\{1/2\pm 1/2\}$) and three $T^*$ states ($\{1,\pm 1\}$ and $\{1,0\}$) with the corresponding level population $n_{S,Sz}$ if at temperature $T_S$ and $N_{S,Sz}$ if at thermal equilibrium with the lattice and the radiation bath at temperature $T_0$ in Table I. 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:

\[
S \leftrightarrow 2D \quad \text{and} \quad 2D \leftrightarrow T^*, \quad (3)
\]

with equilibrium constants:

\[
K_2 = \frac{(a[D])^2}{a[S]} = \exp\left(-\frac{\Delta S_{D}}{2T}\right),
\]

\[
K_3 = \frac{\alpha[D]}{K_1} = \frac{a[T^*](a[D])^2}{\exp\left(\Delta S_{T^*}/2T\right)}, \quad (4)
\]

the doublet lies above the ground state by \( \Delta S_{D}/2 = 3E + 3 \text{ K} \) at room temperature decreasing to 30 K near \( T_c \) and the triplet state lies below the doublet by \( \Delta S_{T^*}/2 \rightarrow \pm 0 \) as \( T \rightarrow T_c \). The activities \( a[i] \) were ascertained from \( D, T^* \Delta S_z = \pm 1 \) ESR intensity measurements, in the absence of saturation above \( T_c \), assuming \( a[S] = 1 \) is the standard state. The rate constant \( k_1 \) was determined previously from the line width broadening of the \( D, \Delta S_z = \pm 1 \) ESR vs \( 1/T \) (figure 1b) as:

\[
\Delta B_{Z,ms} = \text{constant}(k_1 + 1/T_2),
\]

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

where \( (\Delta U/R, A_0 e^{\Delta S/R}) = (111 \text{ K, } 3.5 \times 10^7/\text{s})_{T > T_00}; \quad (11 \text{ K, } 7 \times 10^6/\text{s})_{T < T_00} \) when \( \Delta U \) and \( \Delta S \) are respectively the activation energy and entropy to form the activated states leading to the disappearance of \( D \). The decrease in \( \Delta U \) below \( T_00 \) indicates that there is an easier path for the disappearance of \( D \) whereas the entropy increase, by \( \approx 2R \) above \( T_00 \), suggests that disorder is
introduced by the two possible spin flips for each of the three singlet states formed by antiparallel pairing (above $T_{oo}$) 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, i.e., the triplet states do not provide a relaxation path above $T_{oo}$. Tunneling of D polarons via lattice vibrations pair the spins as $S^*$ states with 1/4 probability and $T^*$ states with 3/4 probability. The separation between the individual bands (figure 5) is determined by the equilibrium constant (4). All the dynamic phenomena depend on the lattice vibrations, e.g., 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 $\Delta E$) satisfy the Boltzmann population distribution, e.g., $n_{S,Sz}/n_{S,Sz} = \exp(-\Delta E/k_BT_S)$ in a saturation experiment the system temperature $T_S$ is greater than the bath temperature $T_0$ and thermal equilibrium is obtained when the Boltzmann temperature approaches $T_0$; the chemical rates, the spin-spin and spin-lattice, and spin-radiation interactions determine the relaxation rates $w(\Delta E)$ between the spin states separated by $\Delta E$ in figure 5. It has been shown that the most efficient processes involve resonant phonons produced via second order Raman processes, i.e., the absorption and emission of phonons at frequencies $\nu_1$ and $\nu_2$ respectively when $\nu_1 - \nu_2 = \nu$, e.g.,

$$E_{S,Sz} + h\nu_{\text{radiation}} = E_{S,Sz}; \ E_{S,Sz} + h\nu_{\text{phonon1}} = E_{\text{intermediate}}; \ E_{\text{intermediate}} - h\nu_{\text{phonon2}} = E_{S,Sz}. \ (6)$$

The phonons are at temperature $T_{\text{phonon}}$ with heat capacity $C_{\text{phonon}}$; they are in contact with the lattice at temperature $T_0$ and infinite heat capacity, and the transition probabilities $w(\Delta E)$ depend on the energy transfer path:
Spin System \((T_s, C_H) \Rightarrow\) Resonant Phonons \((T_{\text{phonon}}, C_{\text{phonon}}) \Rightarrow\) Bath \((T_0, \text{Infinite Heat Capacity})\)

and since \(C_{\text{phonon}} < C_H\) there is a bottleneck when the phonons are involved in phase transitions.

The magnetization relations in the Appendix \((A6)\) obtain the relaxation time for the \(T^*(\Delta S=0)\) transition:

\[
\tau_I(hv) = [w^-(hv)+w^{++}(hv)] + (w(hv/2)+w^+(hv/2))/2 + k_{-1}^{-1}, \quad (7)
\]

i.e., the fourfold \(\tau_I\) increase near 10 K suggests that a phonon bottleneck decreases 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 \(\tau_I\) jump and the Gorter relation \((1)\):

\[
\Delta(\tau_I, T_c)/\tau_I = \Delta C_H/C_H - \Delta \alpha_{\text{ph}}/\alpha_{H} \approx 4,
\]

the data must be compared with heat capacity \(C_p\) taken together with thermal conduction coefficients \(K\) near \(T_c\) where \(C_H\) and \(\alpha\) are the electronic contributions of the spin system to the latter; \(C_p\) and \(K\) are known accurately for cuprate superconductors,\(^1\) \(\Delta C_p(T_c)/C_p=0.03, \Delta K(T<T_c)/K=0.3,^{1,de}\) for \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) but the authors estimate that the electronic contributions are \(\Delta C_e(T_c)/C_e = \Delta K_e(T<T_c)/K_e = 3\) to 4, suggesting that the fractional increase in \(C_e\) and in \(\alpha\) are of the same order of magnitude but that \(\alpha\) increases well below \(T_c\). If the latter applies also to organic superconductors, an increase in \(\alpha\) below \(T_c\) would lead to the \(\tau_I\) decrease in figure 4a.

Other similarities between the organic and the cuprate superconductors may be obtained
from the single crystal ESR (figure 3); the \( T^* \) half field ESR absorption by a single crystal \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) \( (T_c=85 \text{ K})^8 \) observed below \( T_c \) (cooled in \( H=0 \) and in \( H=0 \)) and the absence of D ESR below \( T_c \) suggests that \( k_1 \) is shorter than \( 10^{-10} \text{ s} \). If bipolarons are formed by the \( \pi-\pi \) intermolecular interactions along the triplet axes, the activation energy \( \Delta U \) for the tunneling interactions will be inversely proportional to the corresponding S-S bond order \( (10^{-3})^9 \) then if bipolarons are formed in cuprate superconductors by O-O polarization interactions in the \( \text{CuO}_2 \) plane, the bond order for diagonal sigma bonded O-O pairs \( (10^{-2} \text{ for } <r_{\text{or}},=0.27\text{nm})^{10} \) suggests that \( \Delta U \) is an order of magnitude smaller for the latter. Also if the \( T^* \) gap states contribute to the transport properties then as \( 1/2\Delta_{\text{S,D}} \rightarrow J \) as \( T \rightarrow 0 \text{ K} \), it should be evident in the dependence of such transport properties as the Hall coefficient vs \( T \), as it is in superconducting cuprates.\(^{11}\)

The competition between AF and superconductivity in the organic layer superconductor appears to be similar to that found in superconducting oxides.\(^2\) The AF resonance line width increases as \( T \) decreases below 150 K (figure 2b), indicating that the domain lifetime lifetime decreases to a temperature which allows the appearance of superconductivity at \( T_c \), i.e., the exchange fields measured near 150 K, \( J_{\text{AF}} = 130 \text{ mT} > J \approx 15 \text{ mT} \) suggest that at this temperatures superconductivity is not allowed by the presence of AF domains in the single crystal, however as the lifetime of the latter decreases below \( 10^{-10} \text{ s} \), the superconducting transition is allowed.

The decrease in the bipolaron binding energy \( \Delta_{\text{S,D}}/2 \) (figure 5) with \( T \) suggests that it may continue to decrease down to \( T \rightarrow J \approx 15 \text{ mT} (13 \text{ mK}) \). This will also depend strongly on the lattice vibrations.
Conclusions:

The change in the D, ESR line shape and the appearance of the T*, ΔS=0 ESR identifies the transition temperature where the pairing of doublet polaron states produce a triplet condensate in the organic metal near T_{00}=150±10K. This is of some importance for any theory of superconductivity which predicts the formation of a Bose condensate above T_{c} = 10± K.\textsuperscript{5b} The fact that the T*, ΔS=0 ESR saturates faster than the D with a large increase in τ, near T_{c} suggests that the former are part of the superconducting condensate because they appear to be more sensitive to the changes in the electronic heat capacity at the transition.

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References:


List of Figures:

Figure 1: (BEDT-TTF)$_3$Ta$_2$F$_{11}$, crystallographic axes: $a=1.6683$, $b=1.1928$, $c=1.255\text{nm}$ (a) Structure according to ref. 4b. (b) Temperature dependence of the doublet D ESR absorption line width between the points of maximum slope $\Delta B_{x\text{ms}}$, according to ref. 4a.

Figure 2: (BEDT-TTF)$_3$Ta$_2$F$_{11}$ $B_Z$-LB$_1\parallel$a-axis, $\theta=b\wedge B_z$, $\text{dP/dB}_z$ vs $B_z$ response to the field: (a) Resonance fields satisfying relations (A1) to (A4); energy loss and magnetization oscillations near 3.7 K for sample cooled through $T_c$ in non-zero field (due to flux pinning with a periods of $10^8$ mT (near $B_z=10^2$ mT) to 100 mT (near $B_z=1$ tesla)), these disappear when the sample is cooled in zero field through $T_c$. (b) $T$ dependence of low field AF resonance and appearance of $T^*$, $\Delta S=0$ ESR absorption near $T_{00}$. $T < T_c$: (c) Saturation experiments with the gain normalized to the increase in $B_1$. The saturation factor is given by relation (A5). These show that neither the energy loss nor the magnetization oscillations depend on the incident power and that the $T^*$ saturates faster than the D ESR. (d) D, ESR absorption near $T_{00}$ showing changes in line shape.

Figure 3: Half field $T^*$ ESR for YBa$_2$Cu$_3$O$_{7-\delta}$ below $T_c$ (cooled in $H=0$ and in $H\neq0$)

Figure 4: (BEDT-TTF)$_3$Ta$_2$F$_{11}$: (a) $T^*$, $\Delta S=0$ spin-lattice relaxation time $\tau_1$ vs $T$, evaluated by cw saturation experiments. (b) AF resonance field $B_{z,AF}$ vs angle $\theta=b\wedge B_z$: $\triangledown$, experimental field; $\Box$, calculated field using relation (A3) and $\triangle$, the absolute deviation.

Figure 5: (BEDT-TTF)$_3$Ta$_2$F$_{11}$: Energy level diagram near $B_{z,1/2}$. The insert shows the equilibrium constants the formation of D and $T^*$ vs $T$ from ref. 4a. The double arrows indicate energy level separation whereas the single arrows point to a relaxation process.
Table I: \( \frac{dn}{dt} \) subject to the irradiation of the \( T^* \), \( \Delta S=0 \) transition and chemical rates:\(^a,b,c\)

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\(^a\) \( \frac{dn}{dt} = 0 \) at steady state equilibrium, at \( T_0 \) requires:

\[ w^{++} - w^- \exp(-\hbar v / k_B T_0) = w^+ - w^+ \exp(-\hbar v / 2k_B T_0) = 0 \]

\(^b\) Assuming that the non saturated levels are at \( T_0 \):

\[ n_{||,0} \to N_{||,0}, \quad n_{||,1/2,-1/2} \to N_{||,1/2,-1/2}, \quad n_{||,1/2,1/2} \to N_{||,1/2,1/2} \]

obtains, correct to first order in the Curie-Weiss regime:

\[ \frac{dn_{||,0}}{dt} = w^+ (\hbar v / 2k_B T_s)^2 (T_0 - T_s) / T_0 + k_1 (N_{||,0} - n_{||,0}) \approx 0 \]

or,

\[ w^+ n_{||,1/2,-1/2} = w^- n_{||,1/2,1/2}. \]
Appendix

The spectroscopic identification of the magnetic response uses the principles of magnetic resonance. ESR occurs at resonance fields \( B_{z,i} \) given by:

\[
hv = 2\sqrt{(G_{T^*,0}^2 + E^2)}_{B_{z,i}} = G_{T^*,\pm 1} = G_{D, \pm 1},
\]

\[
G_{T^*,0} = g_T \beta B_{z,T^* 1/2}, \quad G_{D, \pm 1} = g_D \beta B_{z,D}, \quad G_{T^*,\pm 1} = g_T \beta B_{z,T^* 1} \pm (D(3\cos^2 \theta - 1) + E\sin^2 \beta \cos 2\phi) + O^2, \quad E, D \text{ are components of an axial, triplet fine structure tensor at angles } \beta, \phi \text{ to } B_Z. \text{ The } D \text{ and } T^* g_{x,y,z} = 2.00,\]

\( \Delta S_z=\pm 1 \) transitions in a rhombic crystal field have been described previously. The orientation independent, sharp \( T^* \), \( \Delta S=0 \) half field ESR transition appears below \( T_{00} = 150 \text{ K} \) (figure 2b), its transition probability is \( \approx 2(E/G_{T^*,0})^2 \) relative to the \( T^* \), \( \Delta S_z=\pm 1 \) when \( B_{z||B_1||a} \). The observed resonance intensity near \( B_{z,1/2} \) is an order of magnitude weaker than the \( D, g=2, \Delta S_z=\pm 1 \) intensity at \( \approx 150 \text{ K} \); this may be compared to the expected intensity \( 2(E/G_{T^*,0})^2 \approx 2(B_{z,D}^2 - 2B_{z,1/2})/B_{z,1/2} \approx 0.24 \) for the laboratory configuration \( B_{z||B_1||a} \), here the half field transition is allowed because \( B_{z \perp B_1} \) is not parallel to any of the triplet axes. AF resonances with axial symmetry occur at fields added to the domain field along the z direction:

\[
B_{z,AF} = |h\nu/g\beta| \pm |B_{A_z}(2B_E + B_{A_z})|,
\]

\( B_{A_z} = |B_A \cos \theta| \) when \( \theta = B_A ^\wedge B_z \). \( B_A, B_E \) are respectively the aligning field in a given AF domain and the field produced by an exchange interaction \( J_{AF} \) between \( S=1/2 \) states (figure 4b).
The low field, orientation dependent resonance at $B_{z,AF}$ satisfies relation (A2) (figure 2b) for domains aligned parallel to Ta-F-Ta with $g = 1.74$, $\sqrt{(B_E B_A)} = 170 \pm 10$ mT and $B_A = 1.7 \pm 0.1$ mT; $B_E = 220$ mT; $B_{z,AF} = 130$ mT $\pm J_{AF} = 10^2$ mK; $B_{z,AF+}$ is assigned to a broad ($\Delta B_{z,ms} \approx 250$ mT) in figure 2a at temperatures where (A2) is satisfied.

The exchange interaction $J$ gives rise to the splitting of $T^*$ states above the ground singlet $S$ (figure 5); it also determines the line shape of the $D$, ESR $\Delta Sz = \pm 1$ transitions according to the Anderson-Weiss theory:\(5c\) the shape near the center of the line, $B_{z,0}$ is Lorentzian, i.e.,

$$L' = \frac{dP_1}{dB_z} = C/T \left(2\pi \tau_2 \gamma\right)^3 B_1 (B_z-B_{z,0}) [1 + \left(2\pi \gamma \tau_2 (B_z-B_{z,0})\right)^2 + \left(2\pi \gamma \tau_2 \tau_1 B_1\right)^2],$$

$C$ is a constant which depends on the magnetization $M_0$ at the temperature $T$, $\gamma$ is the magnetogyric ratio and $\tau_2$ is the spin-spin or transverse relaxation time. The fields of extreme slope ($L'' = 0$) occur near the center of the line in figure 2d; the increased ESR amplitude in the wings observed below $T_0$ obey a Gaussian distribution function due to an increase in the second moment $<\Delta \nu^2>$ by the exchange interaction $J$, i.e., in the absence of saturation:\(5b,c\)

$$G' = \frac{dP_1}{dB_z} = C'/T \left(2\pi \gamma/<\Delta \nu^2>^{1/2}\right)^3 B_1 (B_z-B_{z,0}) \exp(-2\pi \gamma (B_z-B_{z,0}))^2/(2<\Delta \nu^2>),$$

$$d\mu(G')/dB_z = [1 - (2\pi \gamma (B_z-B_{z,0}))^2/<\Delta \nu^2>]/(B_z-B_{z,0}),$$

allow for an estimate of the second moment experimentally in figure 2d,\(5b,c\) then;

$$J \approx <\Delta \nu^2>/(<\Delta \nu> \approx 15 \text{ mT (or 13 mK) (A3)}$$
near $T_{00}$; $\Delta v_{1/2}/\gamma = 0.36$ mT is the half width and the slope of $G'$ obtains $<\Delta v^2>/\gamma^2 \approx 49$ mT$^2$.

The $T^*$, $\Delta S=0$, $\tau_1$ is evaluated from the $dP/dB_2$ amplitudes at the fields of extreme slopes, $A'_{\text{sample}}$ relative to a reference $A'_{\text{reference}}$. In the Curie-Weiss temperature regime the ratio:

$$ r \equiv \left( T_{\text{sample}} A'_{\text{sample}}/N_{0,\text{sample}}/B_{1,\text{sample}} \right) / \left( T_{\text{reference}} A'_{\text{reference}}/N_{0,\text{reference}}/B_{1,\text{reference}} \right) $$

$$ = \left( 1+(2\pi\gamma)^2 T_{1,\text{reference}} T_{2,\text{reference}} B_{1,\text{reference}}^2 \right)^{3/2} / \left( 1+(2\pi\gamma)^2 T_{1,\text{sample}} T_{2,\text{sample}} B_{1,\text{sample}}^2 \right)^{3/2}, \quad (A4) $$

for Lorentzian lines, is determined with an accuracy of $\Delta r/r \approx 5$%; $B_1/B_{10}$ is known to better than 0.1% accuracy; the reference is the sample (at lowest possible $B_1$) checked with a free radical (1,1'bisbiphenylene2phenylallyl) at room temperature; $N_0$ is the spin concentration. After confirming that $\gamma^2 T_{1,\text{reference}} T_{2,\text{reference}} B_{1,\text{reference}}^2 < 1$; setting $T_{1,\text{sample}} T_{2,\text{sample}} = \tau_1^2$ in (A4) obtains:

$$ 2 \pi \tau_1 = (1/r^{2/3}-1)^{1/2}/\gamma B_1 \pm (2\pi \tau_1 \Delta r/3r \left( 1 - r^{2/3} \right) )^{-1}, \quad (A5) $$

in figure 4a, correct to 3 to 10% when $r=0.25$ to 0.75. The saturation measurements thus give information on the $T^*$, $\Delta S=0$ radiated levels. The population ratios are $N_{l1,l>}/N_{l1,l>=} = \exp(hv/k_B T_0)$ or $n_{l1,l>}/n_{l1,l>=} = \exp(hv/k_B T_S)$ respectively if at thermal equilibrium with the lattice and the radiation bath or when saturated at the corresponding spin temperature; the magnetization $M_{T^*}$ approaches the equilibrium value at $T_0$, $M_{0,T^*}$ via spin-lattice and spin-spin interactions, and the chemical processes (3); the $dn/dt$ for the rates given in Table I obtain the magnetization as a function of both the doublet and triplet state population of the system subject to:

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\[ \frac{d(n_{l,1}\rightarrow n_{l,1})}{dt} = - (2w^{++}n_{l,1}\rightarrow 2w^{-}n_{l,1}) - (w^{+}n_{l,1}\rightarrow w^{-}n_{l,1}) - n_{l,0}(w^{+} - w^{-}) + k_1 \{ (n_{l,2,1}\rightarrow 1)^2 - (n_{l,1,1}\rightarrow 1)^2 \} - k_1(n_{l,1,1}\rightarrow n_{l,1,1}). \]

The half field Ti most efficient relaxation rates \( w^{++}, \ w^{-}, \ w^{+} \) and \( w^{-} \) are induced by \( \hbar \nu \) phonons produced through the motion of ions carrying an electric/magnetic moment and lattice vibrational mode \( q_i = 2\pi \nu / \nu \) when \( \nu \) is the wave velocity. The magnetization relations vs \( T \):\(^{5b}\)

\[ \frac{dM_{T*}}{dT} = (M_{0,T*} - M_{T*}) / \tau_1; \quad M_{T*} = \beta N_{T*} g_{T*} (\hbar \nu / 3k_B T_{T*}); \quad M_{0,T*} = \beta N_{T*} g_{T*} (\hbar \nu / 3k_B T_0) \]

explain the approach to \( T_0 \) where \( w^{++} - w^{-} \exp(-\hbar \nu / k_B T_0) = w^{+} - w^{-} \exp(-\hbar \nu / 2k_B T_0) = 0. \) Then assuming thermal equilibrium for the levels not at resonance with the radiation field obtains to zeroth order, a relation similar to the two level system result:\(^{5b}\)

\[ \frac{d(n_{l,1,1}\rightarrow n_{l,1,1})}{dt} = (n_{l,1,1}\rightarrow n_{l,1,1})(w^{-} - w^{++}) - (w^{+} + w^{++})(n_{l,1,1}\rightarrow n_{l,1,1}) + 0.5 \{ (n_{l,1,1}\rightarrow n_{l,1,1} - n_{l,1,1}\rightarrow N_{l,1,1}) (w^{-} - w^{+}) (n_{l,1,1}\rightarrow n_{l,1,1} - N_{l,1,1}\rightarrow N_{l,1,1}) (w^{-} + w^{+}) \} + k_1(n_{l,1,1}\rightarrow N_{l,1,1}) - (n_{l,1,1}\rightarrow n_{l,1,1}). \]

In the steady state approach to equilibrium, \( \tau_1 \) in relation (2) obtains the working relations:

\[ \frac{d(1/T_s)}{dt} = \{(w^{-} + w^{++}) + (w^{+} + w^{+})/2 + k_1\}(1/T_0 - 1/T_s), \]

\[ \frac{dT_{S,T*}}{dT} = \alpha (T_0 - T_{S,T*})/C_{Hf} = (dM_{T*}/dT) / (dM_{T*}/dT_{S,T*}) = (T_{S,T*}/T_0)(T_0 - T_{S,T*}) / \tau_1, \]

\[ 1/\tau_1 = (w^{-} + w^{++}) + (w^{+} + w^{+})/2 + k_1. \] \( \text{(A6)} \)
(BEDT-TTF)$_3$Ta$_2$F$_{11}$

(a)

(b) Chemical Dynamics by ESR Widths

\[ \ln([\Delta B_{2ms} - \Delta B^*_{2ms}]/\text{gauss}) \]

\[ 0 \quad 0.16 \quad 0.24 \]

\[ 1/T (K^{-1}) \]
(BEDT-TTF)$_3$Ta$_2$F$_{11}$, $\theta=0^\circ$, (20 dB)

(a) ESR/AF/Energy Loss/Magnetization Jumps

<table>
<thead>
<tr>
<th>$B_{z,AF}$</th>
<th>$B_{z,T^*/2}$</th>
<th>$B_{z,D}$</th>
<th>$B_{z,T^*/1}$</th>
<th>$B_{z,AF^+}$</th>
</tr>
</thead>
</table>

75 K

3.7 K cooled in H≠0
magnetization oscillations
cooled in H=0

Energy Loss

3.7 K

T*
(BEDT-TTF)$_3$Ta$_2$F$_{11}$, $\theta=0^\circ$

(b) Low Field ESR (25 dB) above $T_c$
(BEDT-TTF)$_3$Ta$_2$F$_{11}$, $\theta=20^\circ$, 3.7K ESR

(c) $T^*:\quad$ 

\[ \Delta S = 0 \]

-10 dB

25 dB

$r = 0.177$

D: 

\[ \Delta S_z = \pm 1 \]

-10 dB

25 dB

$r = 0.35$
(BEDT-TTF)$_3$Ta$_2$F$_{11}$, $\theta=70^\circ$, (20 dB)

(d) D, ESR above and below $T_{00}$

\[ \theta : C = 3403.705 \text{ SI/N} \]

180 K

\[ \theta : C = 3406.108 \text{ SI/N} \]

170 K

\[ \theta : C = 3405.898 \text{ SI/N} \]

150 K
$\left(\text{CH}_2\right)_2\text{S}_2\text{C}_2\text{S}_2\text{C}=\text{CS}_2\text{C}_2\text{S}_2(\text{CH}_2)_2\text{Ta}_2\text{F}_{11}, \ T<T_c\approx 10 \text{ K}$

$\text{Y}_{0.2}\text{Ca}_{0.8}(\text{SrO})_2(\text{CuO}_2)_2(\text{Tl}_{0.5}\text{Pb}_{0.5}\text{O}), \ T_c(\approx 108) \pm 20\text{ K}$
(BEDT-TTF)$_3$Ta$_2$F$_{11}$ Energy Level Diagram in $B_{z,1/2}$

$D_{\text{Polaron,}1/2,1/2}$ Band:
$\downarrow w^-(1/2 hv) \quad \uparrow w^+(1/2 hv) \quad 1/4 k_1 \rightarrow S^*_{\text{Bipolaron Band}}$

$D_{\text{Polaron,}1/2,-1/2}$ Band:

$\frac{1}{2} \Delta S-D$

$(10^3 K)$

$\bullet: \frac{1}{2} \Delta_{T^*-D}$

$T^*_\text{Bipolaron,1,1} \rightarrow \text{Band}$

$\downarrow \downarrow w^-(hv) \quad \uparrow w^+(1/2 hv)$

$T^*_\text{Bipolaron,1,0} \rightarrow \text{Band}$

$\downarrow w^-(1/2 hv) \quad \uparrow \uparrow w^{++}(hv)$

$T^*_\text{Bipolaron,1,-1} \rightarrow \text{Band}$

$\downarrow (\text{forbidden})$

Fast (allowed)