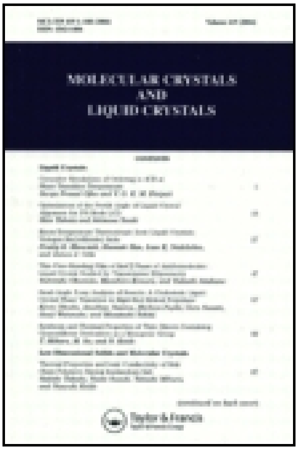

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Phase Transitions in $(Tmttf)_2BF_4$

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PHASE TRANSITIONS IN $(TMTTF)_2BF_4$

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Abstract A semiconductor-model analysis of the temperature dependence of conductivity under pressure reveales a phase transition due to gap enhancement in $(TMTTF)_2BF_4$. A corresponding transition around 80K at ambient pressure is found in both conductivity and thermopower. Absence of susceptibility anisotropy indicates a nonmagnetic state below 40K.

In $(TMTTF)_2BF_4$ at ambient pressure, two phase transitions have been reported so far. The conductivity shows a broad maximum at a temperature T_m around 200 K.[1,2] Below T_m the conductivity decreases more or less exponentially with temperature. (Fig. 1) It was suggested that the metal-semiconductor transition occurs around T_m due to a rapid increase in dimerization there.[3] However, the constant value of the thermopower over the temperature range from 300 down to about 100 K (Fig. 2 and Ref. 4) indicates that there is no phase transition in this range.

On the other hand, a strong change of the magnetic susceptibility and a small specific heat anomaly clearly indicate the presence of a phase transition at 41 K.[1] A large increase of the infrared vibronic absorption associated with dimerization of the TMTTF stacks are observed below about 40 K.[5] X-ray diffuse scattering revealed unusual and intricate features.[6] A diffuse spot with $\underline{q}$=(1/2,1/2,1/2) condenses below about 40 K, whose precurser was observed above 40 and up to more than 100 K.

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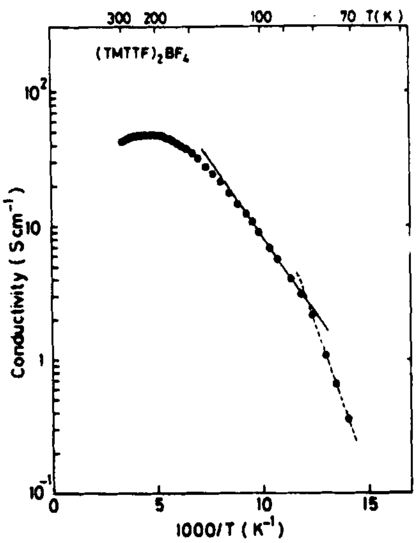
As already pointed out, "resistance jumps", i.e. a sudden increase or decrease of the absolute value of the resistivity usually occur during the thermal cycling of the samples.[7] The data plotted in Fig. 1 were obtained after correction of this effect. A trial to fit a theoretical model to α vs T is therefore venturous. However, it was pointed out that this effect can be suppressed by the application of high pressure.[8] No resistance jump was observed during cooling under pressure higher than 5 kb. Thus, we believe we can safely try to fit a semiconductor model to σ vs T of $(TMTTF)_2BF_4$ under pressure.

It has been shown that a "metal-like" semiconductor model can account well for σ vs T of $Qn(TCNQ)_2$ and other 1/4-filled-band materials over a wide range of temperatures including a simillar shallow maximum.[9] The conductivity is proportional to the product of an activated carrier concentration with an activation energy, Δ, $n \propto \exp(-\Delta/T)$, and a strongly temperature dependent mobility $\mu \propto T^{-\alpha}$, where the value of α depends on the scattering mechanism.



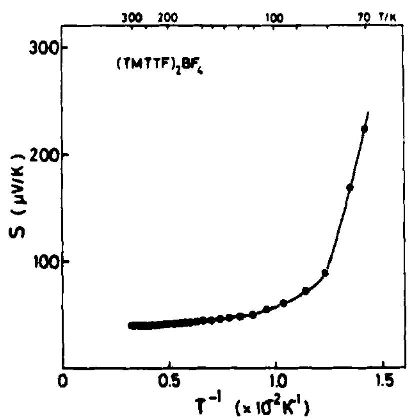


FIGURE 1 (Left) Temperature dependence of conductivity at ambient pressure.
FIGURE 2 (Right) Temperature dependence of thermopower.

That is,

$$\sigma(T) = ne\mu = \sigma_o T^{-\alpha} \exp(-\Delta/T) \qquad (1)$$

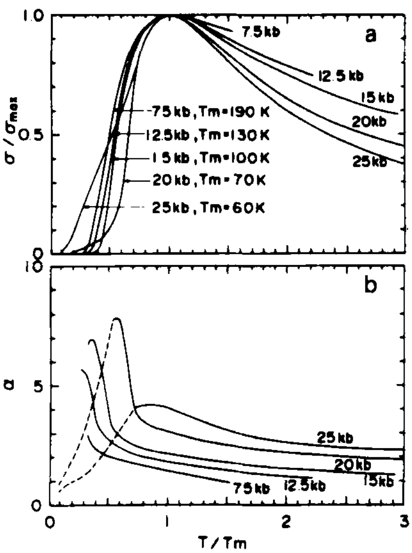
where σ_o is a constant. Equation (1) reduces to a normalized form

$$\sigma(T)/\sigma_{max} = [(T/T_m) \exp\{(T_m/T)-1\}]^{-\alpha};\ T_m = \Delta/\alpha \qquad (2)$$

with only one fitting parameter, α. Thus we can calculate α as a function of temperature from

$$\alpha(T) = \ell n\,\{\sigma(T)/\sigma_{max}\}/\{1 - (T_m/T) - \ell n(T/T_m)\} \qquad (3)$$

using the experimental values for $\sigma(T)$, σ_{max} and T_m, as shown in Figure 3. Since α obtained in this manner for various applied pressure shows a fairly weak temperature dependence from 300 K down to temperatures well below T_m, the semiconductor model seems applicable in these temperature ranges. The observed weak temperature dependence may reflect the fact that the dimerization gap decreases at high T due to lattice vibration.[4] The critical temperature at which α shows a sharp rise, indicating a sudden enhancement of the gap, is plotted by closed circles in Figure 4 as a function of pressure. Interestingly, we observed a simillar



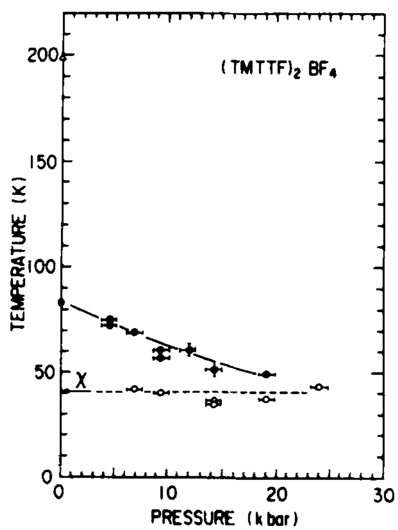


FIGURE 3 (Left) Normalized conductivity under pressure versus normalized temperature (a) and calculated α (b).
FIGURE 4 (Right) Transition temperature versus pressure.

gap enhancement around 80 K at ambient pressure in both conductivity and thermopower (see Figs. 1 and 2). Open circles in Figure 4 correspond to temperatures where α started to decrease as the temperature was lowered. These temperatures are around 40 K, and appear almost independent of pressure.

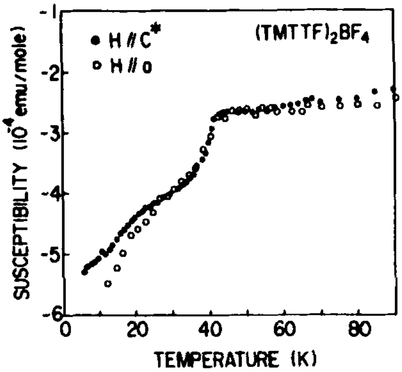


FIGURE 5 Static magnetic susceptibility along a and c^* axes of a $(TMTTF)_2BF_4$ single crystal. (The value along a axis is shifted for comparison.)

Finally, absence of susceptibility anisotropy shown in Figure 5 indicates a nonmagnetic ground state rather than the SDW state below 40 K. A shoulder around 25 K may be related to the condensation of a set of diffuse peaks reported in Ref. 6.

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