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PHASE TRANSITIONS IN (TMTTF) 2BF4

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<u>Abstract</u> A semiconductor-model analysis of the temperature dependence of conductivity under pressure reveales a phase transition due to gap enhancement in (TMTTF)₂BF₄. 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 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. 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. 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 α vs T of (TMTTF) ${}_{2}BF_{\Delta}$ 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, $\Delta,$ n $^{\alpha}$ exp(- Δ/T), and a strongly temperature dependent mobility $\mu^{\alpha}T^{-\alpha}$, where the value of α depends on the scattering mechanism.

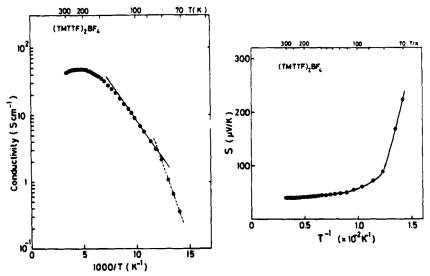


FIGURE 1 (Left) Temperature dependence of conductivity at ambient pressure.

FIGURE 2 (Right) Temperature dependence of thermopower.

That is,

$$\sigma(T) = ne_{\mu} = \sigma_{0} T^{-\alpha} \exp(-\Delta/T)$$
 (1)

where σ_0 is a constant. Equation (1) reduces to a normalized form $\sigma(T)/\sigma_{max} = \left[(T/T_m) \exp\{ (T_m/T) - 1 \} \right]^{-\alpha}; T_m = \Delta/\alpha$ (2)

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

$$\alpha(T) = \ln \{\sigma(T)/\sigma_{max}\}/\{1 - (T_m/T) - \ln(T/T_m)\}$$
 (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. 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

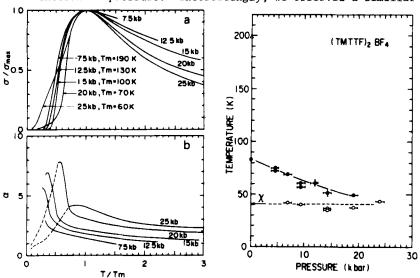


FIGURE 3 (Left) Normalized conductivity under pressure versus normalized temperature (a) and calculated α (b). FIGURE 4 (Right) Transition temperature versus pressure.

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.

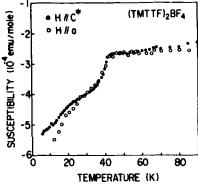


FIGURE 5 Static magnetic susceptibility along a and c^* axes of a (TMTTF) ${}_2^{\rm BF}{}_4$ single crystal.

(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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