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Short Communication

**Competition between insulating and superconducting states in  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl : pressure effect**

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**Abstract.** — The pressure effect on the resistance behavior of the organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl is studied. At ambient pressure it has an insulating ground state, however at a modest pressure of 150 bar superconductivity with  $T_c$  near 12 K appears and coexists with high-temperature semiconducting regime in pressure range up to 340 bar, where the later is fully suppressed and superconducting transition temperature reaches the maximum value (midpoint 12.7 K, onset 13.4 K). Under further pressure increasing  $T_c$  strongly decreases. The details of the resistance behavior at different pressures and the relation between superconducting and insulating states are discussed.

Recently, Williams *et al.* [1] reported on the discovery of an organic superconductor,  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl, with  $T_c = 12.5$  K. Under the ambient pressure this salt exhibits semiconducting behavior, and superconductivity with the highest  $T_c$  for an organic material is recorded at pressure of 300 bar after the suppression of a semiconductor-semiconductor transition near 40 K.

Such an extreme effect of the moderate pressure on the ground state as well as the close neighborhood of semiconducting and superconducting phases in this compound are very puzzling. In order to study the relationship between superconductivity and semiconducting (insulating) instability in  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl and their mutual influence, we have carried out the simultaneous investigation of pressure effect on both the normal state resistivity and superconductivity.

Single crystals of  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl have been obtained by electrochemical oxidation of BEDT-TTF (2 mmol/l) in 1,1,2 trichloroethane under constant current conditions with a current 0.44 mA. A mixture of 18-crown-6-ether, CuCl and NaN(CN)<sub>2</sub> (5 mmol/l each) has been used as an electrolyte.

Four probe electrical resistivity measurements under pressure have been carried out using the "Unipress" helium gas pressure apparatus. Pressure values were measured by a manganine gauge which was placed at the entrance of a capillary coupling the gas compressor and a pressure ves-

sel. Temperatures were measured with a germanium thermometer affixed to the exterior of the pressure vessel at the sample level.

The resistance vs. temperature behavior,  $R(T)$ , at the various pressures is illustrated in figures 1, 2. At  $P = 150$  bar resistance vs. temperature curve shows remarkable changes near 170 and 75 K. Moreover, the low-temperature part is found quite unexpected. Instead of a final insulating transition it shows a weak maximum near 31 K which is followed by remarkable resistance decrease to 25 K. On further cooling the resistance sharply increases, indicating insulating transition. However at 12.8 K the complete superconducting transition starts immediately from the semiconducting regime. Note that we have found no evidence of the preceding metallic state restoration (or formation). Instead, the direct competition of the insulating and superconducting phases occurs, indicating, therefore, their puzzling proximity.

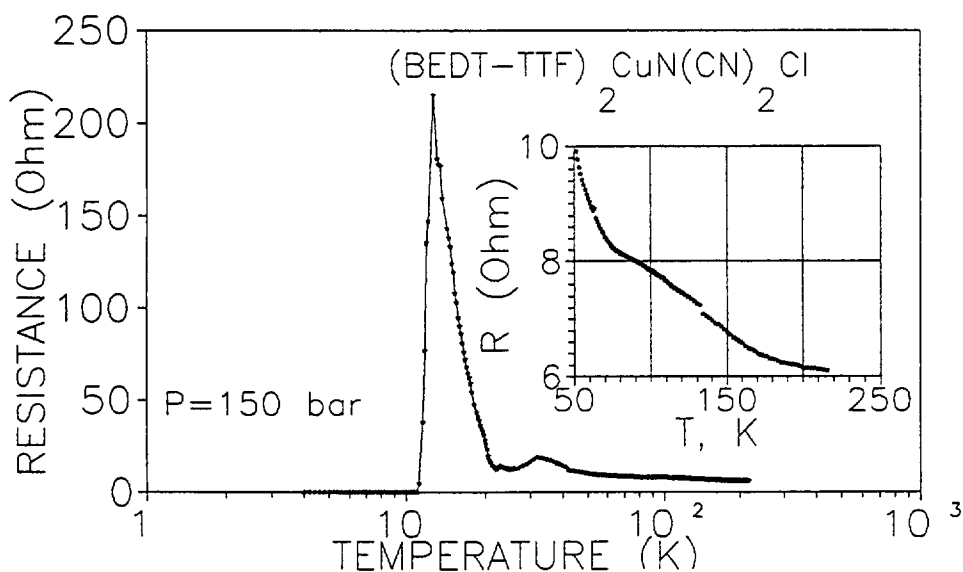


Fig. 1. — Temperature dependence of resistance of  $\kappa$ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Cl crystal at pressure  $P = 150$  bar, inset shows high-temperature part.

The origin of this phenomenon as well as the tendency of  $\kappa$ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Cl to be insulating are not understood. A similar behavior was found earlier for (TMTSF) $_2$ AsF $_6$  crystals, unstable against Spin Density Waves (SDW) formation [2]. Assuming that SDW or CDW (Charge Density Waves) ordering occur in  $\kappa$ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Cl, it is tempting to attribute the anomalous resistance decreasing near 25 K, just before the insulating phase transition, to sliding incommensurate SDW or CDW contribution into the conductivity (For a review see [3]). Then insulating transition following this resistance drop may be attributed to some possible pinning process.

As is seen from figure 2 the semiconductor-like behavior is rapidly suppressed under higher pressures, while the superconducting transition temperature strongly increases at a rate of 5 K/kbar. At the pressure of 250 bar the resistance exhibits transition from semiconducting to metallic state in region near 80 K. In the region of 35-60 K we note another remarkable anomaly – an extremely sharp resistance drop under cooling. With further temperature decreasing the resistance becomes

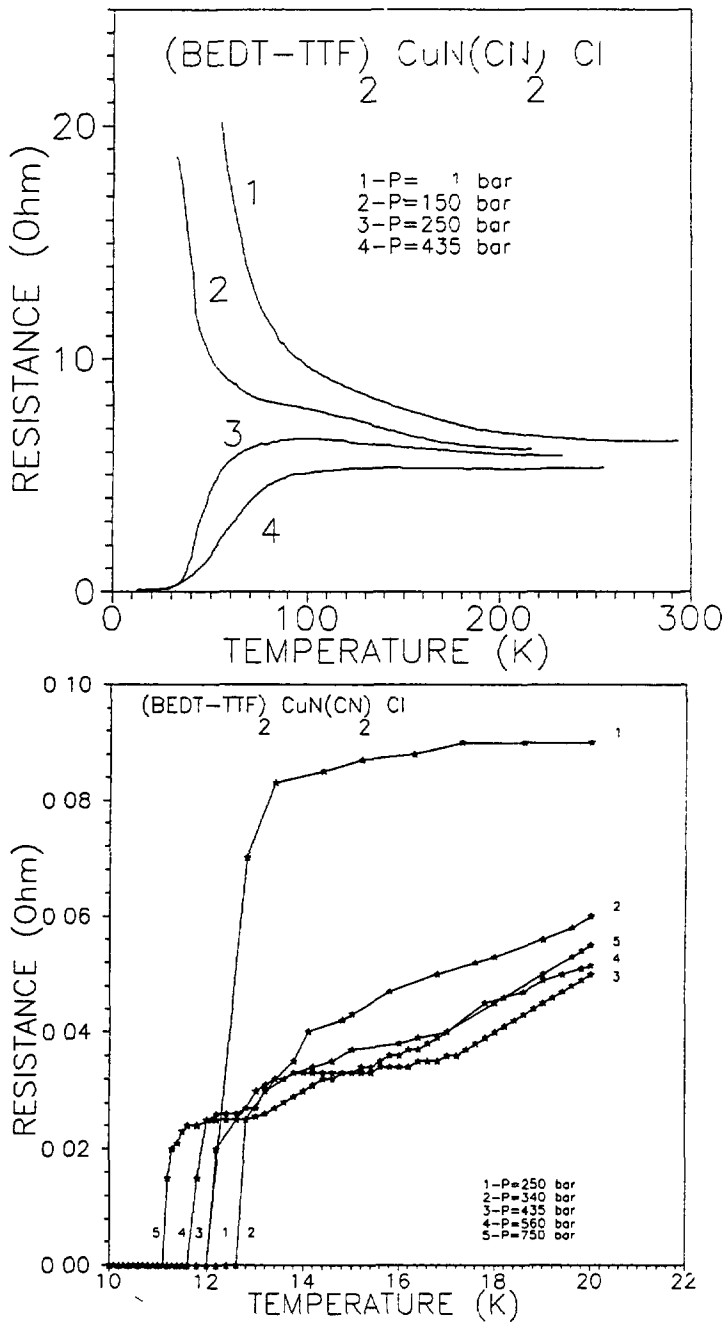


Fig. 2. — Temperature dependence of the resistance of  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl at different pressures a) general view; b) low-temperature part.

slightly depending on the temperature down to the region of the superconducting transition. At  $P = 340$  bar, in pressure range where the semiconducting behavior is strongly suppressed,  $T_c$  reaches the maximum value of 12.7 K (onset at 13.4 K). Under further pressurization only metal-

lic behavior is observed, and  $T_c$  sharply decreases at a rate of  $-3.6$  K/kbar.

The data on the pressure dependence of  $T_c$  we presented and reported by Williams *et al.* [1] are summarized in figure 3. Note a good coincidence in a pressure range  $P > 340$  bar. At this threshold pressure the remarkable acceleration in conductivity vs. pressure growth is also seen at 65 K, contrary to linear increase at higher temperatures (Fig. 4).

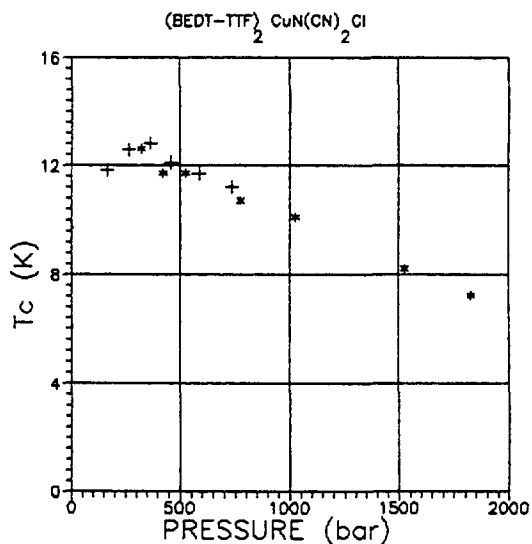


Fig 3 — Pressure dependence of superconducting transition temperature of  $\kappa$ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Cl samples. Symbols (+) denote resistivity midpoint values we reported, symbols (\*) represent the data reported by Williams *et al.* [1].

In conclusion, the influence of helium gas hydrostatic pressure on resistivity of  $\kappa$ -(BEDT-TTF) $_2$ CuN(CN) $_2$ Cl was studied. Superconducting transition has been found at modest pressures  $P > 150$  bar where it starts immediately from the semiconducting regime and  $T_c$  strongly increases with pressure. Remarkable conductivity growth near 25-30 K at 150 bar and near 35-70 K at 250 bar was also observed. At  $P = 340$  bar metallic state is stabilized and  $T_c$  shows the maximum value (midpoint 12.7 K, resistivity onset 13.4 K). Conductivity vs. pressure dependence at  $T = 65$  K shows pronounced change under the same pressure of 300-400 bar. Further pressure increasing causes rapid drop of  $T_c$  at a rate of  $-3.6$  K/kbar.

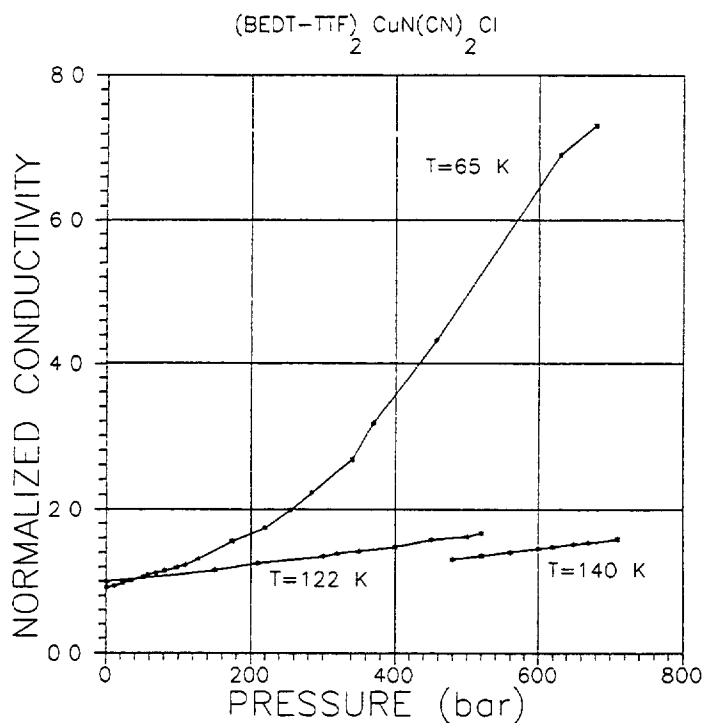


Fig 4 — Pressure dependence of  $\kappa$ -(BEDT-TTF)<sub>2</sub>CuN(CN)<sub>2</sub>Cl conductivity at temperatures 140 K, 122 K, and 65 K.

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