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Temperature Dependence of the Electrical Conductivity of Single Crystal Quinolinium $(TCNQ)_2$

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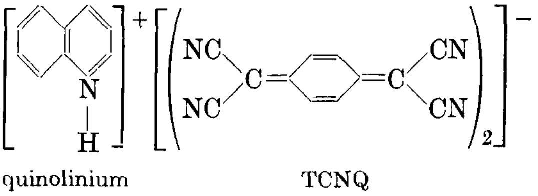
Previous electrical,⁽¹⁾ optical⁽²⁾ and magnetic susceptibility⁽³⁾ data of the complex anion-radical salt quinolinium $(TCNQ)_2$ have been interpreted in terms of a model in which the close face to face stacking of TCNQ molecules allows the formally unpaired electron (one unpaired electron per two TCNQ molecules) to be completely delocalized over the entire TCNQ array producing a strongly degenerate electron gas. Specific evidence for this model comes from several sources: the X-ray data for other 1 : 2 complexes (e.g. triethylammonium $(TCNQ)_2$,⁽⁴⁾ tetraphenylphosphonium $(TCNQ)_2$⁽⁵⁾) show a face to face stacking of TCNQ with a closer than van der Waals separation between the molecular planes (no X-ray data are available for the quinolinium salt); the electrical conductivity for this complex is very high at room temperature ($\sigma = 100\ \Omega^{-1}\ \mathrm{cm}^{-1}$)¹; the magnetic susceptibility is temperature independent from about 50 °K to 300 °K which has been interpreted as being due to Pauli paramagnetism⁽³⁾ and the EPR intensity between 103 °K and room temperature is also temperature independent,⁽⁶⁾ a result consistent with the temperature independent paramagnetism.



There are, however, a number of features of the proposed degenerate model for which there is conflicting evidence. For instance, Kondow, Siratori and Inokuchi(7) find an absorption edge at 36.5 cm^{-1} in the room temperature far infrared absorption spectrum (although they did not see this edge at 1.5 °K).(8) In addition, Siratori and Kondow(8,9) find that the magnetic susceptibility is temperature dependent from 77 °K to room temperature contrary to the results of Kepler.(3)

Since no extended measurements of the temperature dependence of the conductivity have been reported for quinolinium $(TCNQ)_2$ and in light of the negative results found with regard to the presence of superconductivity in these materials,(10) it was of interest to us to examine the electrical properties of these salts in more detail.

Figure 1 shows the results of measurements of the electrical conductivity along the needle axis on two single crystals of quinolinium $(TCNQ)_2$ under 30 microns of helium from 77 to 370 °K. Four probe measurements were used (two for current and two for potential) in order to eliminate contact resistance. Typical sample dimensions were $2.0 \times 0.06 \times 0.06$ mm^3. In order to reduce strain and prevent

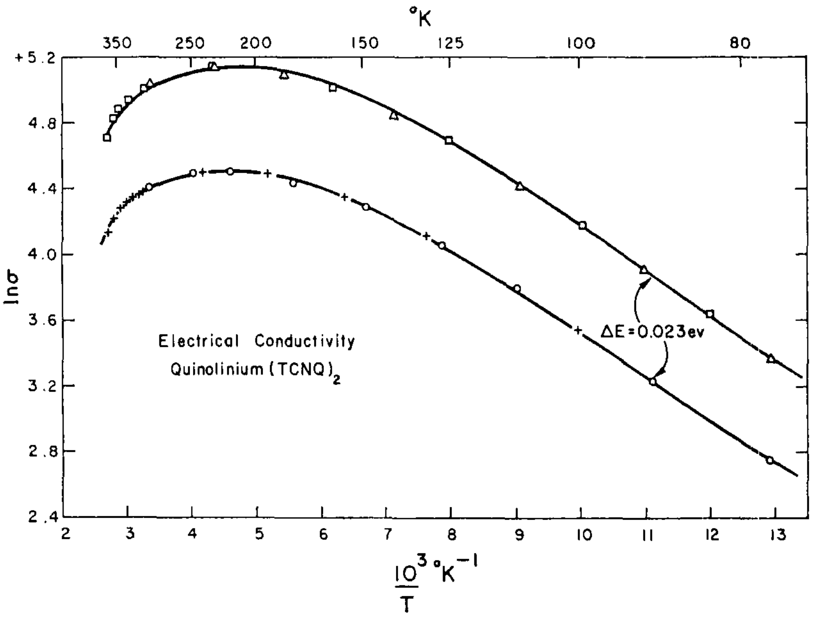


Figure 1. Natural logarithm of the conductivity (in Ω^{-1} cm^{-1}) along the needle axis versus inverse temperature for two single crystals of quinolinium $(TCNQ)_2$. O—cooling, +—heating, sample III–63; △—cooling, □—heating, sample III–64. Cooling curves were determined first.

the crystals from cracking upon cooling and heating, it was necessary to partially suspend the crystals between ½ mil (0.0005 inch) diameter gold plated tungsten wires which also served as current and potential probes. Dupont silver paint 4929 was used as the wetting agent between crystal and wire probes. Both cooling and heating curves are shown; no hysteresis was found although for temperatures in excess of 100 °C, erratic non-reproducible behavior was observed, most likely indicating sample decomposition.

As can be seen from Fig. 1 the conductivity (in Ω^{-1} cm^{-1}) increases from 77 °K up, reaching a maximum at about 223 °K and then begins to fall above this temperature. The low temperature activation energy, ΔE is 0.023 eV based on the equation $\sigma = \sigma_0 e^{-\Delta E/kT}$.

These conductivity results do not support a strong degeneracy model for quinolinium $(TCNQ)_2$. Our preliminary measurements of the Seebeck coefficient S, on single crystals over the same temperature range show a room temperature value of -74 uv/°K indicative of electron carriers. There also appears to be a minimum in S occurring between 200 and 230 °K which would indicate that the conductivity may be associated with two types of charge carriers (electrons with different mobilities, for instance).

While the general shape of ln σ of Fig. 1 is what one would expect if there were an impurity donor 0.023 eV below a conduction band with the high temperature part of the curve being in the donor exhaustion region, the fact that " exhaustion " sets in at the same temperature for both samples would tend to eliminate a random impurity concentration as the cause for the activation energy. We conclude rather that the conductivity is due to the intrinsic properties of the anion radical itself.

We can also not exclude a hopping model with a mobility which has an activation energy of 0.023 eV or less. For $kT > 0.023$ eV the pre-exponential factor (which usually varies as T^{-n}) in an activated mobility model(11) will dominate so that the mobility will decrease with increasing temperature, a result which has been discussed by Emin for correlated small polaron motion.(12)

It is thus possible that the conductivity temperature dependence is due to small polaron hopping with a gradual transition from uncorrelated to correlated small polaron motion with increasing temperature.

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