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ABSTRACT

It is demonstrated that the magnetic and electric properties of N-methyl-quinolinium $(TCNQ)_2$ are similar to that found in other well conducting complex TCNQ salts.

АННОТАЦИЯ

Доказывается, что магнитные и электрические свойства н-метил-квинолиниума $(TCNQ)_2$ аналогичны другим хорошо проводящим комплексным солям TCNQ.

KIVONAT

Megmutatjuk, hogy az N-methyl-quinolinium $(TCNQ)_2$ mágneses és elektromos tulajdonságai hasonlóak azokhoz, amelyeket más jólvezető complex TCNQ sókon találtak.

Among the complex salts of tetracyanoquinodimethan (TCNQ) only two, acrinidium $(TCNQ)_2$ and quinolinium $(TCNQ)_2$ belong to the highly conducting class having well documented anomalous resistivity behaviour and peculiar magnetic susceptibility[1]. We demonstrate, that the N-methyl-quinolinium salt $NMeQn(TCNQ)_2$ has similar magnetic and electric properties.

$NMeQn(TCNQ)_2$ was prepared from high purity N-methyl-quinolinium iodide and TCNQ. The boiling solution of 0.95 g N-methylquinolinium-iodide in 15 ml acetonitrile was added to a solution of 1.5 g TCNQ in 150 ml acetonitrile. Blue-black needles (typical dimensions: 5x0.1x0.05 mm) separated immediately, after two hours the product was filtered at room temperature and washed with acetonitrile and ether[2].

The temperature dependence of the dc and microwave conductivity is shown in Fig. 1a. At low temperatures the conductivity is well represented by $\sigma = \sigma_0 \exp\{-\Delta E/kT\}$ with $\sigma_0 = 30\,\Omega^{-1}\mathrm{cm}^{-1}$, and $\Delta E = 0.07$ eV. The activation energy is in agreement with that obtained by Siemons et al[3] on compressed material. The dc conductivity starts to flatten out at around 300°K and the microwave conductivity shows a weak maximum at this temperature, see insert of Fig 1a. A similar behaviour is observed in $Qn(TCNQ)_2$ at around 200°K[1,4]. The overall behaviour of the conductivity is rather similar in the two salts, the N-methyl derivative has a maximum conductivity smaller by a factor of two, the temperature where the conductivity has a maximum, and the activation energy is increased by about the same factor, the only difference with respect to $Qn(TCNQ)_2$ is the despressed frequency dependence of the conductivity. Here the dc and the microwave conductivity have essentially the same temperature dependence except the high temperatures, around $300^{o}K$. In this respect $NMeQn(TCNQ)_2$ reflects the behaviour observed in less conducting salts like $TEA(TCNQ)_2$[1]. The temperature dependence of the microwave dielectric constant is shown in Fig 1b. The large dielectric constant, which increases with increasing temperature is again a general property of the well conducting complexes[1] and similarly to the conductivity both the magnitude and temperature dependence is somewhat than that of the typical good conductors.

The temperature dependence of the magnetic susceptibility is shown in Fig 2, where we have also plotted the susceptibility of the quinolinium[5] salt. The susceptibility was also measured by the Shumaker-Slichter method at room temperature, giving $\chi_{spin} = 3.7\ 10^{-4}$ emu/mole, this leads to a diamagnetic contribution to the static susceptibility $\chi_{dia} = -4.2$ emu/mole. The overall behaviour of the susceptibility of the quinolinium and the N-methyl quinolinium salts are again similar. We have argued before[4] that in $Qn(TCNQ)_2$ the low temperature upturn is due to spins localized at chain ends and the intrinsic susceptibility (due to infinite chains) is smoothly decreasing with decreasing temperature going to zero as $T\rightarrow 0$ suggesting a singlet ground state. The low and high temperature part of the susceptibility is well separated here, and even without the substraction of the low temperature upturn it is evident that the intrinsic susceptibility is neither Pauli type, nor is similar to a simple singlet-triplet excitation found of the less conducting salts[6]. The narrow (of about 250 mG) and nearly temperature independent ESR linewidth is also characteristic to the complex salts with high conductivity.

With these electric and magnetic properties NMeQn$(TCNQ)_2$ represents an intermediate between the highly conducting and less conducting complex TCNQ salts. Some of its properties, in particular the maximum in the conductivity, the large dielectric constant and the temperature dependence of the susceptibility resemble of the highly conducting group, the absence of the dispersion of the conductivity is parallel to that of the intermediate conductors.

It is expected that in complex TCNQ salts long range Coulomb correlation effects play an important role[7] together with interactions of the electrons on the TCNQ chains with the donor molecules[8], these interations determine the band gap and the band width. Disorder effects then result in band tailing and in a mobility gap separating localized from delocalized states[9]. Clearly for large bandgap disorder plays a minor role as evidenced by the small dielectric constant, negligible disperison of the conductivity together with the well defined energy for the collective magnetic excitation, observed in less conducting TCNQ salts. In good conductors, characterized by small band gaps the large dielectric constant and microwave conductivity gives evidence of strong band tailing, the susceptibility is characteristic to a smeared out excitation spectrum. It is not surprising therefore, that NMeQn$(TCNQ)_2$ where the gap - as determined from the conductivity - is between that of the good and intermediate conductors, has features resembling both in one or other respect. It is not understood at present how the substitution of -H with the $-CH_3$ groups in the donor influences the cooperative electric and magnetic properties, futher systematic investigations may answer this question.

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2 Analysis: C calculated 73.9 %, found 73.6 %,
N calculated 22.8 %, found 23.3 %

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CAPTIONS

Fig 1a. Temperature dependence of the conductivity of $NMeQn(TCNQ)_2$. The insert shows the microwave conductivity around $300^\circ K$.

1b. Temperature dependence of the microwave dielectric constant.

Fig 2. Temperature dependence of the susceptibility of $NMeQn(TCNQ)_2$ and of $Qn(TCNQ)_2$.

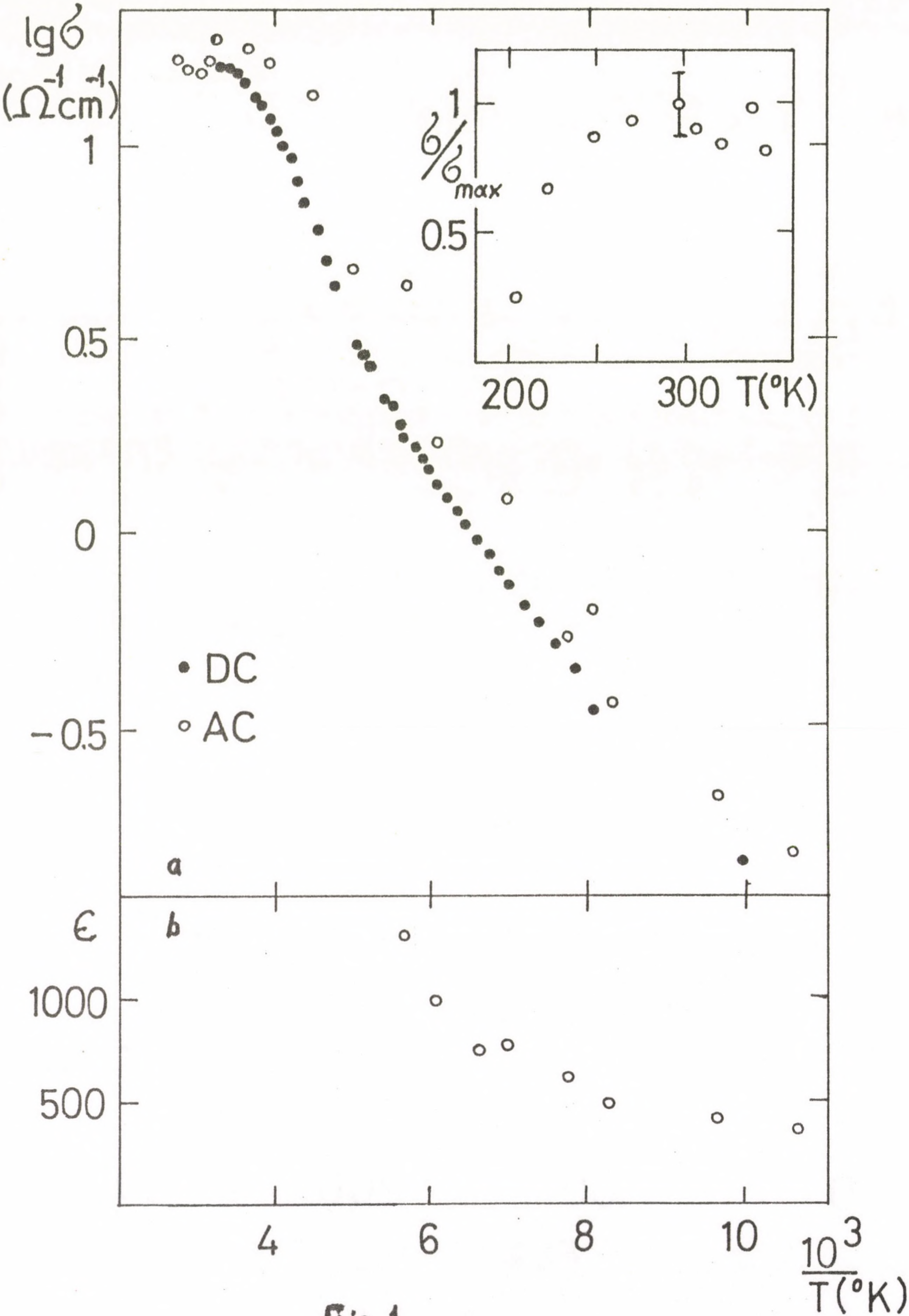
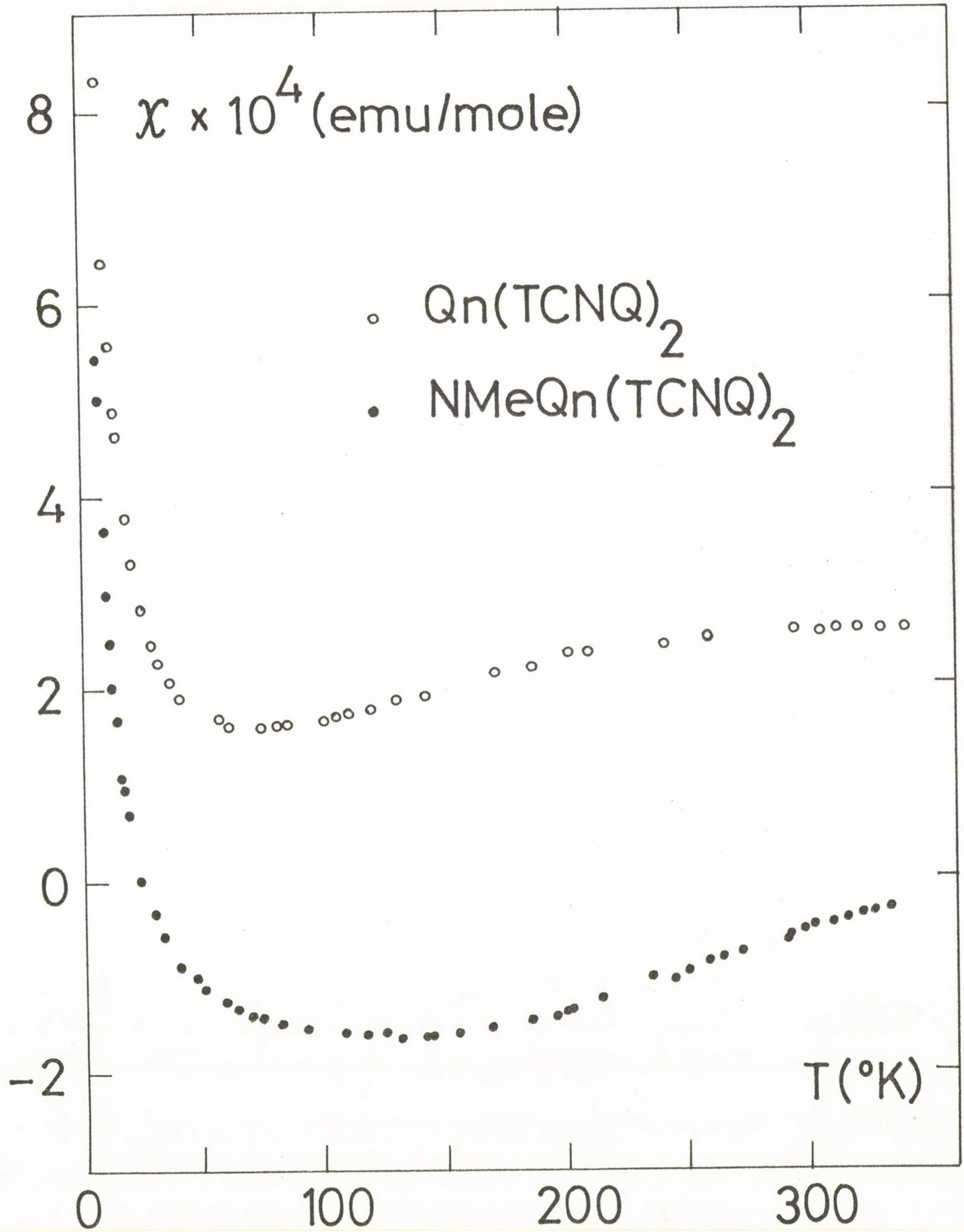

lg σ
(Ω⁻¹cm⁻¹)
1
0.5
0
−0.5
• DC
∘ AC
a
σ/σmax
1
0.5
200
300 T(°K)
ε
b
1000
500
4
6
8
10
10³/T(°K)

Fig 1.



$\chi \times 10^4$ (emu/mole)
Qn(TCNQ)$_2$
NMeQn(TCNQ)$_2$
T(°K)
8
6
4
2
0
−2
0
100
200
300

Fig 2

62.224

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