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The conductivity of alloyed radical anion salts: 2,5-disubstituted DCNQI's with copper-counterions


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Abstract. — We have performed conductivity measurements on a series of binary and ternary copper-salts from differently substituted R, R’ - N, N’-dicyano-quinonediiimines (DCNQI’s). At room temperature they all have a high conductivity, which is preserved partly down to the lowest temperatures. In comparison with the (unalloyed) single complex crystals in these alloys disorder effects shift phase transition temperatures and reduce the magnitudes of the conductivity. In two cases dips of the T-dependent conductivity appear below 50 K. They are explained by a metal-semiconductor transition accompanied by a reentrance into the metallic state at even lower temperatures, in analogy to similar results on (2,5-Me, Me-DCNQI)2Cu under applied pressure.

1. Introduction.

A large variety of radical anion salts from 2,5-disubstituted DCNQI’s with metallic counterions has been synthesized until now. Due to the slope of their conductivity and their magnetic properties [1, 2] these salts can be separated into two groups.

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(a) The « non-copper salts » (2-Rl-5-R2_DCNQI)zM with M = Li+, Na+, K+, Rb+, Tl+, Ag+ or even with NH+ as counterions can all be characterized as 1d systems [1]. This is seen from their characteristic temperature dependences of the conductivity and of the ESR lines, which are generally narrow [1, 2].

(b) Although the basic crystal structure is not altered considerably, the Cu-salts stand apart from all others. Their conductivity at room temperature is higher (up to an order of magnitude) and in case of (2,5-Me, Me-DCNQI )2Cu for example, a stable metallic state is found down to the lowest temperatures investigated [3], resulting in a conductivity of $5 \times 10^5 \text{S cm}^{-1}$. For all Cu-salts, no ESR signal is seen in the high temperature region, indicating a strong SOC-contribution to the ESR-linewidth, similar to common 3d metals. These exceptional features of the Cu-salts can be explained by an admixture of Cu-states to the 1d conduction band on the anion stack, as has been directly demonstrated by UV-photoelectron spectroscopy [4]. As a consequence of this admixture, the limitations of 1d transport (localization of the charge carriers by impurities or correlation effects etc.) are removed (by-passed) by an additional channel for interstack charge carrier transport over N-Cu-N bridges.

Slight geometric changes in the coordination sphere of Cu however, introduced by different substituents (Cl or Br instead of a methyl group), temperature or pressure (70 bar in the case of (2,5-Me, Me-DCNQI )2Cu) [5] affect the contribution of Cu-states to the conduction band and can cause a metal-semiconductor transition.

To get further insight into the influence of changes in the geometrical structure at the Cu-ion sites on the physical properties of the Cu-salts, we have investigated a series of Cu-salt alloys with differently substituted DCNQI's. As is commonly known from alloys, increasing disorder not only results in additional scattering, but critical phenomena and instabilities are expected to be influenced as well. In this paper we present mainly conductivity results on different alloys, because the conductivity is most sensitive on the alterations mentioned above.

2. Experimental.

The alloys investigated are composed of 2-R1-5-R2-DCNQI's with different substituents R1, R2 = Cl, Br, I, CH3 and OCH3 and Cu as counterion. For simplification the abbreviation ($R_1, R_2$)2Cu will be used in the following.

Single crystals of the alloys were grown electrochemically according to reference [3]. Equal portions of the components (100-200 $\mu$mol) together with 200-300 $\mu$mol CuBr2 were solved in 60 ml acetonitrile. The current was kept between 30 and 50 $\mu$A (current density : 170-300 $\mu$A/cm²). After several days we obtained shiny black needles with a typical length of 5-15 mm and a thickness of 5-15 $\mu$m.

The composition of these crystals, as far as possible, was calculated from the elemental analysis of carbon, hydrogen and nitrogen. The results for the binary alloys are listed in table I. In three cases the composition is yet unsure, because the results of elemental analysis were not reproducible.
By the same method described above we were able to grow crystals of the ternary alloys (Cl, Me)\textsubscript{0.67} (Br, Me)\textsubscript{0.67} (I, Me)\textsubscript{0.67}Cu and (Me, Me)\textsubscript{0.4} (Br, Me)\textsubscript{0.8} (I, Me)\textsubscript{0.8}Cu.

The conductivity measurements were performed by a standard four probe technique. Silver strips were evaporated perpendicular to the crystal axis and contacts were attached with silver paint.

3. Results.

The temperature dependent conductivities of the alloys are given in figures 1-3. Via their different temperature dependence towards 4 K, these alloys can be separated into two groups:

(a) alloys with a highly conductive state at low temperatures

All investigated binary alloys containing the compound (I, Me)\textsubscript{2}Cu, with the exception of (I, Me) (Cl, Me)Cu, stay highly conductive down to 4 K (Fig. 1). This also holds for the alloy of the components (Me, Me)\textsubscript{2}Cu and (OMe, OMe)\textsubscript{2}Cu [6]. The non alloyed crystals of both components are outstanding as far as the magnitude and the temperature dependence of the conductivity is concerned. The ratio \(\sigma (3.8 \text{ K})/\sigma (300 \text{ K})\) for (Me, Me)\textsubscript{2}Cu for example is of the order 500. This increase of conductivity is considerably reduced for all alloys listed above. The typical ratio of conductivity between 3.8 K and room temperature is of the order 10 or even lower. The binary alloys of (I, Me)\textsubscript{2}Cu with (Me, Me)\textsubscript{2}Cu and (Br, Me)\textsubscript{2}Cu below 100 K exhibit anomalies in \(\sigma (T)\). In both cases a conductivity minimum appears at 50 K. Below 50 K \(\sigma\) rises again and finally saturates at 10 K (Fig. 5);

(b) alloys with a semiconductive state at low temperatures

Though they all have high conductivities at room temperature, their quantitative temperature dependences vary somewhat. Three of them exhibit a very high room temperature conductivity (300-700 S\text{cm}\textsuperscript{-1}) and concomitantly their \(\sigma (T)\)-curve resembles the \(T\)-dependent conductivity of the unalloyed salts (Cl, Me)\textsubscript{2}Cu and (Br, Me)\textsubscript{2}Cu (Fig. 2). But the sharp phase transition found for the latter salts is more or less softened for these alloys and partly the phase transition temperatures do not coincide with those of the pure salts (195 K and 150 K). For the alloy (Cl, Me)\textsubscript{1} (Br, Me)\textsubscript{1}Cu the transition temperature of 180 K lies in between these values, whereas a shift of \(T_c\) to even lower temperatures (~130 K) is found for

### Table I. — Binary alloys of the Cu-salts.

<table>
<thead>
<tr>
<th>Component 1</th>
<th>%</th>
<th>Component 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me, Me</td>
<td>25</td>
<td>Cl, Me</td>
<td>75</td>
</tr>
<tr>
<td>Me, Me</td>
<td>25</td>
<td>Br, Me</td>
<td>75</td>
</tr>
<tr>
<td>Me, Me</td>
<td>30</td>
<td>I, Me</td>
<td>70</td>
</tr>
<tr>
<td>Cl, Me</td>
<td>40</td>
<td>Br, Me</td>
<td>60</td>
</tr>
<tr>
<td>Br, Me</td>
<td>60</td>
<td>I, Me</td>
<td>40</td>
</tr>
<tr>
<td>Cl, Me</td>
<td>75</td>
<td>I, Me</td>
<td>25</td>
</tr>
<tr>
<td>Me, Me</td>
<td>—</td>
<td>OMe, OMe</td>
<td>—</td>
</tr>
<tr>
<td>Me, OMe</td>
<td>—</td>
<td>I, Me</td>
<td>—</td>
</tr>
<tr>
<td>I, Me</td>
<td>—</td>
<td>OMe, OMe</td>
<td>—</td>
</tr>
</tbody>
</table>
Fig. 1. — $T$-dependent conductivity of those Cu-salt alloys which are highly conductive at low temperatures.

Fig. 2. — $T$-dependent conductivity of the Cu-salt alloys with a sharp metal-semiconductor transition.

Fig. 3. — $T$-dependent conductivity of Cu-salt alloys having an extremely softened metal-semiconductor transition.
(I, Me)(Cl, Me)Cu. The phase transition of the ternary alloy (Cl, Me)_{0.67}(Br, Me)_{0.67} (I, Me)_{0.67}Cu is close to that of (Br, Me)_{2}Cu. A room temperature conductivity of 200 Scm^{-1} and an extreme softening of the phase transition is present for the second ternary alloy investigated (Me, Me)_{0.4}(Br, Me)_{0.8}(I, Me)_{0.8}Cu (Fig. 3). The T-dependent conductivity in this case approaches to the curves, which are characteristic for all non copper salts of DCNQI’s [1, 2]. This similarity is even more pronounced for the alloys of (Me, Me)_{2}Cu with (Cl, Me)_{2}Cu and (Br, Me)_{2}Cu if we take into account their room temperature conductivity of \sim 100 Scm^{-1} and their rounded \sigma(T)-curve as well.

4. Discussion.

Before discussing the results on alloys, we want to give a brief summary of the models of charge transport, which were applied for the explanation of the conductivity of unalloyed DCNQI-salts with metallic counterions. Due to their crystal structure (segregated stacks of DCNQI-molecules and metal-ions) in all these salts (copper and non-copper salts as well) a conduction band is expected on the anion stack by the overlap of the 1T-orbitals of adjacent DCNQI-molecules (LUMO-band). In contrary the bond distances \(d(M-M)\) on the metal ion stack would be much too large (378-397 pm) for electron transport, even if an open shell configuration is assumed.

In case of Ag^+, Ti^+, NH_4^+ and the alkali-ions Li^+, Na^+, K^+, Rb^+ the transport properties as well as the magnetic properties [1] can be explained by a 1d conduction band on the anion stack solely, with all the problems of 1d: i.e. localization of the charge carriers by smallest disorder introduced by defects in the molecular stack for example [7]. Similarly electron-electron correlations can localize the electrons by the formation of a pinned charge-density-wave [8] and finally 1d systems are unstable against a lattice distortion, which can be induced by electron-phonon interaction [9].

These features of 1d systems are evident from the physical properties of the Ag-salts (the most investigated non copper salts) [1, 2]. Additionally, first UV-photoelectron-spectra (UPS) from (Me, Me)_{2}Ag have revealed a vanishing density of states at the Fermi level [10]. This finding is characteristic for low dimensional organic conductors and indicates, that the Fermi-level lies within an energy gap as it is the case in semiconductors.

For these salts the conductivity can be approximated by the expression [11]:

\[ \sigma(T) = A \cdot e^{-\Delta/kT} \cdot T^{-a} \]  

(1)

\(T^{-a}\) represents the temperature dependent mobility and \(e^{-\Delta/kT}\) gives an activated concentration of mobile charge carriers. In figure 4, \(\sigma(T)\) of (Br, Me)_{2}Ag and the fit according to equation (1) is shown for demonstration. The activated charge carrier concentration can be explained by the 1d features discussed above. Disorder, by the formation of a mobility gap [11] and electron-electron interactions in a quarter filled band (\(\rho = 0.5\)), due to the Coulombic repulsion \(V_1\) between electrons on neighboring sites can induce a gap for the charge carriers. In the latter case an activation energy of the order \(\Delta \approx V_1 - 2t_1\) (\(t_1\) : transfer integral) is expected [12].

The situation drastically changes, when copper is used as counterion. In this case UPS reveals a non vanishing density of states near the Fermi level [4]. This finding was attributed to an admixture of Cu(3d) states to the \(p\pi\)-conduction band on the anion stack. From crystal structure considerations, such an admixture is not unexpected. The short M-N bond distances (in case of the Cu-salts (198-200 pm) indicate strong coordination between Cu^+ and the cyano group [13]. The resulting higher dimensional molecular overlap overrides the limitations of 1d transport discussed above. Consequently the room temperature conductivity of (Me, Me)_{2}Cu

\(\sigma(T) = A \cdot e^{-\Delta/kT} \cdot T^{-a} \)
Fig. 4. — $T$-dependent conductivity of unalloyed Cu-salts. For comparison $\sigma (T)$ of (Br, Me)$_2$Ag and a
fit according to equation (1) is given too ($\alpha = 2$, $\Delta = 584$ K).

for example is an order of magnitude higher as compared to the former salts and the metallic
state is stabilized down to the lowest temperatures investigated.

This admixture depends strongly on the local symmetry of the Cu coordination sphere. For
(Cl, Me)$_2$Cu and (Br, Me)$_2$Cu the distortion of the tetrahedral coordination sphere is
enhanced as compared to (Me, Me)$_2$Cu. Consequently the contribution of Cu(3d) states near
the Fermi level as seen by UPS [4] is reduced and a sharp metal-semiconductor transition is
apparent at 195 K and at 150 K in the latter case (Fig. 4), respectively. In a similar manner the
conductivity of (Me, Me)$_2$Cu is affected by external pressure, which seems to reduce the local
symmetry as well. A pressure of only 100 bar is sufficient to introduce a phase transition at
$T \leq 50$ K [5]. By increasing pressure up to 8.5 kbar, the metal-semiconductor transition
temperature is shifted towards room temperature. The magnitude of the resistance jump is
high when the transition occurs at low temperatures, but only a small reduction is found for a
transition at high temperature.

Summarizing, phase transition of Cu-salts can be attributed to a switching off of the N-Cu-
N bridges, if the local symmetry of the Cu-ions is altered by pressure or by introduction of
substituents on the DCNQI-molecule. The systems become 1d and behave in this manner
below $T_c$. This explanation is in accordance with the band structure calculations of Kobayashi
et al. [6]. Assuming a negligible distortion of the tetrahedral coordination of the Cu-atom in
(Me, Me)$_2$Cu they found a multi-Fermi surface, which should be insensitive to 1d-instabilities
and localization effects. If the distortion increases, by applied pressure or by substitution of a
methyl group by Cl or Br, the crystal field splitting of the Cu(3d) orbitals increases, reducing
their contribution to the conduction band. Finally, due to a change of the lattice constants at
the phase transition, the Cu(3d)-admixture vanishes.
For the alloys of the Cu-salts it is expected, that the distortion of the tetrahedral coordination is not homogeneous over the whole sample. This type of disorder is deduced from a softening of the metal-semiconductor transition, as will be discussed later.

Usually, disorder in alloys of ordinary metals, can be described by Matthiessen's rule:

\[ \frac{1}{\sigma(T)} = \rho(T) = \rho_D + \rho_P(T). \]  \hspace{1cm} (2)

Here \( \rho_P(T) \) stands for the temperature dependent part of the resistivity due to electron-phonon scattering. The constant term \( \rho_D \) results from electron scattering by defects and limits the increase of conductivity at low temperatures. On alloying different metals disorder is enhanced and therefore \( \rho_D \) as well. Consequently the conductivity at low temperatures is reduced for the alloys as compared to pure metals.

The influence of increased disorder is also visible from the results of our conductivity measurements on alloyed Cu-salts of DCNQI's. The alloys, which are still conducting at low temperatures, exhibit only a moderate increase of the conductivity towards 4 K, as compared to the best unalloyed Cu-salts.

The temperature dependent conductivity of the salt (I, Me)\(_2\)Cu, having only one sort of anion, but which is asymmetrically substituted, also fits into this picture. From a simple comparison of the Van der Waals radii of the two substituents CH\(_3\) (200 pm) and I (215 pm) it is expected, that disorder is already introduced into this salt by the asymmetric substitution of a methyl group by Iodine. A further analogy between (I, Me)\(_2\)Cu and its alloys with (Me, Me)\(_2\)Cu and (Br, Me)\(_2\)Cu is evident from figure 5. The pronounced dip in \( \sigma(T) \), which is observable for these two alloys below 100 K, is also weakly present in the pure salt. To illustrate this finding, we have fitted the expected regular \( T \)-dependent conductivity according to Matthiessen's rule. The constant part of the resistivity \( \rho_D \) for this calculation was taken

![Log-log plot of the T-dependent conductivity of unalloyed and alloyed Cu-salts. The drawn lines were calculated according to equation (2).](image-url)
from the experimental data at the lowest temperatures and the $T$-dependent part $\rho_p(T)$ was assumed to be proportional $T^{-\alpha}$ ($\alpha \approx 2.2$). The resulting curves are plotted as solid lines in figure 5. This approximation seems justified, since the same fit reproduces the experimental $\sigma(T)$-data for $(\text{Me}, \text{Me})_2\text{Cu}$ too. The deviation between theory and experiment at about 20 K is easily explained by scattering theory in a range, where the phonon density is no longer linear in $T$ [4].

A key for the explanation of the dips in $\sigma(T)$ of $(\text{I}, \text{Me})_{1.4}(\text{Me}, \text{Me})_{0.6}\text{Cu}$ and $(\text{I}, \text{Me})_{0.8}(\text{Br}, \text{Me})_{1.2}\text{Cu}$ are the pressure works of Tomič et al. on $(\text{Me}, \text{Me})_2\text{Cu}$ at low applied pressures of up to 300 bar [5]. Under these conditions besides the normal pressure induced phase transition, a reentrance into the metallic state was observed at very low temperatures [5]. The $\sigma(T)$-curve at 75 bar for example appears quite similar to our results in figure 5. Therefore we assume, that the same mechanism is responsible for the pressure induced phase transition of $(\text{Me}, \text{Me})_2\text{Cu}$ and the observed anomalies discussed above as well. If we exchange the meaning of external pressure by disorder («internal pressure») we can easily explain the $\sigma(T)$-curves in figure 5 by a shift of the $p-T$ phase diagram of $(\text{Me}, \text{Me})_2\text{Cu}$ towards lower pressure.

In case of that alloys, which exhibit a semiconducting state at low temperatures, the distortion of the tetrahedral symmetry is expected to be more pronounced even at room temperature, similar as has been confirmed by UPS-experiments for the pure salts of asymmetrically substituted DCNQI's $(\text{Cl}, \text{Me})_2\text{Cu}$ and $(\text{Br}, \text{Me})_2\text{Cu}$ [4]. Consequently the phase transition is shifted towards higher temperatures and no reentrant behaviour appears.

The jump of the conductivity at the phase transition, in case of the alloys, is not as sharp, as for the pure salts. This can be explained by the disorder, which is present in the alloys, as has been shown by preliminary X-ray crystal structure investigations [15]. Due to this disorder the distortion of the coordination sphere around Cu is not homogeneous over the whole sample and the phase transition therefore is smeared to some extent.

Still puzzling is the temperature dependent conductivity of the alloys of $(\text{Me}, \text{Me})_2\text{Cu}$ with $(\text{Br}, \text{Me})_2\text{Cu}$ and $(\text{Cl}, \text{Me})_2\text{Cu}$. In both cases the temperature dependent conductivity is similar to the $\sigma(T)$-curves measured on the 1d non copper salts, implying a strong distortion of the Cu-tetrahedron. From a simple comparison of the Van der Waals radii of Br (195 pm) for example and CH$_3$ (200 pm) such a strong distortion is unexpected for the corresponding alloy. Further experiments (UPS, X-ray crystal structure investigations, static paramagnetic susceptibility measurements, etc.) will be necessary to elucidate this question.

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