# Optically Reversed Peierls Transition in Crystals of Cu(dicyanoquinonediimine)₂

F. O. Karutz, J. U. von Schütz, H. Wachtel, and H. C. Wolf

*3. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany*
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A fast photoinduced transient switching of partly deuterated Cu(2,5-dimethyl-N,N′-dicyanoquinonediimine)₂ [Cu(DCNQI)₂] radical ion salt crystals is analyzed as a reversed Peierls transition. Switching from the insulating state into the conducting state is performed on a time scale below 20 ps. Conductivity indirectly proves that the Peierls distortion of the insulating phase is efficiently canceled by photoexcitation. Evaluation of the electrical transients shows that the switched volume can be at least 100 times larger than the directly photoexcited part of the crystals. We propose a reversible structural change which is induced by an acoustic wave traveling through large parts of the sample volume. [S0031-9007(98)06448-5]

One-dimensional metals are known to undergo a metal-insulator phase transition at low temperature which first was discussed by Peierls [1]. Radical ion salts of 2,5-dimethyl-N,N′- dicyanoquinonediimine (DCNQI, molecular structure, see inset of Fig. 4 shown later) [2] have attracted considerable interest because of their high metallic conductivities in spite of their stacked structures. The protonated Cu salt [$h_8$-Cu(DCNQI)₂] reaches up to 500 000 S cm⁻¹ at $T = 4.2$ K [3]. Its conduction mechanism is thought to be modified from one-dimensional to quasi-three-dimensional by the admixture of Cu 3$d$ states [4]. Changing the counterions (e.g., Ag, Tl, and alkali metals) a quasi-one-dimensional conductivity is observed corresponding to the structure of segregated stacks, which are present in both the Cu salts and the alkali salts [5].

Deuteration of the six methyl hydrogens (abbreviated by $d_6$) provokes a structural metal-insulator phase transition in the corresponding Cu salt $d_6$-Cu(DCNQI)₂ [6] taking place around 78 K. The transition is also accompanied by a change from mixed valence of Cu$^{1.3+}$ (metallic) to a trimerized form . . . Cu⁺Cu²⁺Cu⁺ . . . (insulating). Alloyed crystals containing a mixture of $h_8$ and $d_6$ (70%:30%) $h_8/d_6$-Cu(DCNQI)₂ undergo the metal-insulator transition at ≈60 K, and they recover from the insulating state below 30 K, showing a reentry of metallic conductivity [7]; cf. Fig. 1. As these phase transitions can be influenced by temperature, external pressure, and light [8], the question arises of how fast they are and which mechanisms are responsible.

Optically induced phase transitions have recently been investigated in inorganic materials, e.g., the charge-ordered state in a perovskite manganite was shown to collapse due to photocarrier injection [9]. Organic charge transfer compounds (e.g., tetrathiafulvalene-chloranil [10]) were studied by photoreflectance, yielding a phase transition taking place within roughly 400 ps [11]. In contrast, we study the photoinduced phase transition by measuring the conductivity, thus probing the whole conducting volume. The electrical fields applied in the present experiments are

as small as 2 V cm⁻¹ in the vicinity of phase transition temperatures. In the insulating phase (operating point op2) fields up to $E = 100$ V cm⁻¹ are used.

The experiments were carried out at characteristic operating points (op1, op2, op3) which are indicated in Fig. 1, where the temperature dependence of the dc conductivity of the $h_8/d_6$-(70%:30%)-Cu(DCNQI)₂ salt is given. Simultaneously, the linear thermal expansion of the $c$ axis was determined using a capacitive dilatometer. The structural nature of the phase transition is demonstrated by the contraction (0.4% with respect to standard conditions $T = 273$ K, $p = 1$ bar). The large hysteresis proves a first order transition.

Most of this contribution deals with the $h_8/d_6$ alloys, but we also present data of genuine $d_6$-Cu(DCNQI)₂ and $h_8$-Li(DCNQI)₂ (cf. Table I). Apart from the lack of a reentry at op3, the $d_6$ salts show a behavior [12] similar to the alloy, however, the phase transition appears at a
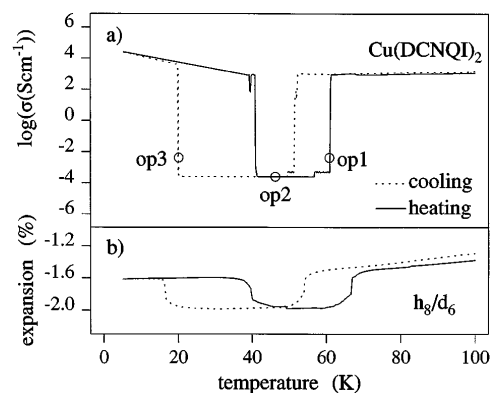


FIG. 1. (a) Temperature dependence of conductivity of $h_8/d_6$-(70%/30%)-Cu(DCNQI)₂ salts. Please note the logarithmic scale. Three operating points are schematically indicated as op1, op2, and op3 (reentry point) which are used for the optical experiments. The precise temperatures are given in the figure captions. The system shows a large hysteresis. (b) Simultaneous dilatometry proves the structural nature of the phase transition in $h_8/d_6$-(70%/30%)-Cu(DCNQI)₂ salts.

TABLE I. DCNQI salts investigated. The sequence of phases is quoted for cooling from 300 to 4 K. $T_c$ and $T_r$ are the approximate phase transition temperature and the reentry temperature.

| Abbreviation | Phases | $T_c$, $T_r$ (K) |
|---|---|---|
| $d_6$-Cu(DCNQI)$_2$ | metal, insul. | 78, $\cdots$ |
| $h_8/d_6$-Cu(DCNQI)$_2$ | metal, insul., metal | 60, 30 |
| $h_8$-Li(DCNQI)$_2$ | metal, semicond. | 100, $\cdots$ |

slightly higher temperature. $h_8$-Li(DCNQI)$_2$ displays a thermally activated conductivity below 100 K and in this respect differs considerably from the Cu salts in spite of their common structure (space group $I4_1/a$).

The optical experiments were performed on needle-like crystals (diameter 0.2 mm, length 1–5 mm). The excitation was provided by a Nd:YAG laser (BMI 502 DNS/DPS) which optionally pumped an optical parametric generator in the 30 ps mode. Wavelength dependent experiments were performed at constant pulse energy. The samples were homogeneously illuminated between the contacts using a cylindrical lens. In order to perform electrical measurements, single crystals were glued to the coaxial contacts of the sample holder by carbon paste (Dotite XC-12 black). The samples, the geometry of fixture, and low-temperature semirigid cables were optimized for maximum bandwidth using a HP 79 829 microwave transition analyzer. The fastest transients electrically recorded with the setup are $<$20 ps.

The short-time transient current response of $d_6$-Cu(DCNQI)$_2$ at operating point op2 is given in Fig. 2(b). The sample is in the insulating state, and the transient corresponds to conventional photoconductivity. The initial rise time (10% to 90%) of the current equals
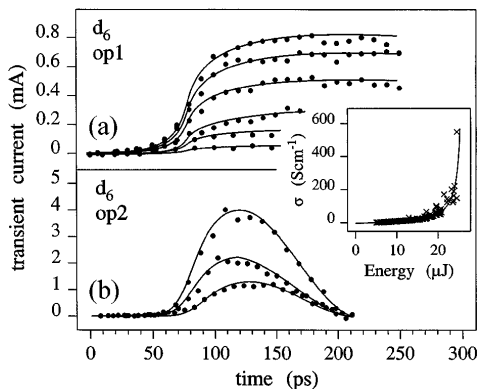
30 ps. It is at least a factor of 30 faster than the change of reflectivity in the mixed stack TTF-CA compound [11]. The decay time is also fast and amounts to 50 ps. The fast onset also holds for the other operating points and the other samples, e.g., $h_8/d_6$ alloys as well as a fast component of $h_8$-Li(DCNQI)$_2$ (not shown). However, the decay in the deuterated Cu salts and alloys at operating point op1 shows a completely different behavior [Fig. 2(a)]. There is no decay on the ps scale but the first rise is followed by a long-term tail which reaches decay times up to 300 ns at sufficiently high excitation.

The long-time transients of $h_8/d_6$-Cu(DCNQI)$_2$ at all operating points are shown in Figs. 3(a)–3(c) for different pulse intensities. Similar transients are obtained for $d_6$-Cu(DCNQI)$_2$ at op1 and op2 (not shown). All transients of Fig. 3 are filtered with 0.5 GHz bandwidth. Under strong illumination the metallic conductivity (broken line) of the crystal is reached by photoexcitation at op1 and op3. The high current response can be observed only close to the phase transition temperatures, while at op2 a smaller signal is detected, even in spite of a higher $E$
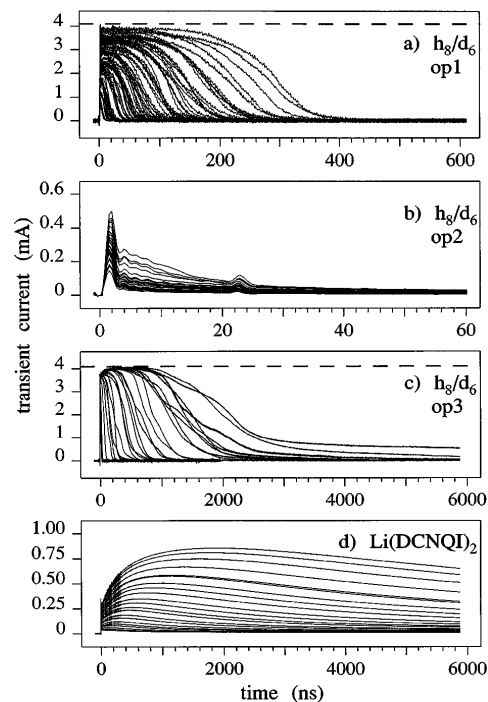


FIG. 2. Short-time transient current response of $d_6$-Cu(DCNQI)$_2$. Excitation at 18 750 cm$^{-1}$. (a) Operating point op1: $T = 78$ K, $E = 2$ V cm$^{-1}$. Excitation 4, 4.5, 5.5, 6, 6.5, and 7.5 $\mu$J/pulse corresponding to $(0.44{-}0.83) \times 10^8$ W cm$^{-2}$. The inset shows the peak conductivity $\sigma$ as a function of the incident laser pulse energy at the same conditions. (b) Operating point op2: $T = 54$ K, $E = 100$ V cm$^{-1}$. Excitation 9.5, 12.5, and 19 $\mu$J/pulse corresponding to $(1.06{-}2.12) \times 10^8$ W cm$^{-2}$.



FIG. 3. Long-time transient current response of $h_8/d_6$-Cu(DCNQI)$_2$ at 18 750 cm$^{-1}$ excitation. Please note different time scales. (a) Operating point op1: $T = 55$ K. $E = $ V cm$^{-1}$. Excitation 5–40 $\mu$J/pulse corresponding to $(0.67{-}5.33) \times 10^8$ W cm$^{-2}$. (b) Operating point op2: $T = 50$ K. $E = 30$ V cm$^{-1}$. Excitation 45–115 $\mu$J/pulse corresponding to $(6{-}15.3) \times 10^8$ W cm$^{-2}$. (c) Operating point op3: $T = 28$ K. $E = 3$ V cm$^{-1}$. Excitation 5–60 $\mu$J/pulse corresponding to $(0.67{-}8) \times 10^8$ W cm$^{-2}$. (d) Transients of low-dimensional Li(DCNQI)$_2$: $T = 37$ K. $E = 13$ V cm$^{-1}$. Excitation 20–180 $\mu$J/pulse corresponding to $(2.1{-}19) \times 10^8$ W cm$^{-2}$.

field applied. This small signal is composed of a short peak and a slower tail. $h_8$-Li(DCNQI)$_2$ also shows a second component with slow onset and decay as given in Fig. 3(d).

The transient current signal exhibits a linear field dependence for both $d_6$ and $h_8/d_6$ alloyed crystals. The range investigated was between $-30$ to $50 \, V \, cm^{-1}$ (operating points op1, op3) and 0 to $50 \, V \, cm^{-1}$, as well as $100 \, V \, cm^{-1}$ [op2, Fig. 2(b)]. This is clearly contrasted by the nonlinear behavior of the Li salt at moderate fields ($-25$ to $25 \, V \, cm^{-1}$). The transient current sets in at a lower light intensity which can be extrapolated to $3 \, \mu J/$pulse. The transient conductivity increases superlinearly with the pulse energy. An example is given for the peak conductivity of a $d_6$ crystal at op1 (Fig. 2, inset). Saturation is reached at $30 \, \mu J/$pulse, where the dark conductivity of the highly conducting state of the crystal is obtained (not shown). Further increase in pulse energy results only in prolonged duration of the on state and a slower decay. Persistent switching into the conducting state occurs at op1 above $30 \, \mu J/$pulse, whereas at op2 and op3 the intensity can be increased until irreversible changes occur above $200 \, \mu J/$pulse.

The wavelength dependence of the maximum transient current [Fig. 4(a)] reaches its peak value at $15\,000 \, cm^{-1}$ for samples of $d_6$-Cu(DCNQI)$_2$. Spectra of other Cu salts are similar. The peak current response at op1 agrees fairly well with the molar extinction of the DCNQI$^-$ anion [Fig. 4(b)]. In addition, there is a shoulder at $11\,500 \, cm^{-1}$. At operating point op2, the response is weaker even with increased $E$ field, and the feature at $11\,500 \, cm^{-1}$ has gained relative weight. It is ascribed
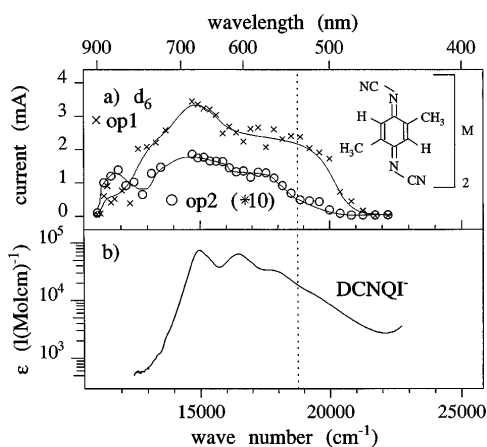
to aggregates (anionic/neutral) in analogy with Hubbard [13]. Figure 4(b) contains the molar extinction of DCNQI$^-$ anions in CH$_3$CN solution. In contrast to this spectrum the transmission data of Cu(DCNQI)$_2$ derived from thin film measurements is unstructured as well as the reflection data [14,15].

Starting the discussion, we briefly summarize the striking features of our experiments on the Cu salts: (i) Onset and decay of "conventional" photoconductivity are extremely fast at op2. (ii) Close to the phase transition temperatures (op1, op3) the decay slows down; the slower it is the higher the optical excitation pulse energy. (iii) Strong excitation yields transient conductivities which require the participation of most of the crystal volume. (iv) The spectral response corresponds to the DCNQI$^-$ anion.

We now discuss operating point op2. It is assumed that the pulse response of our samples is dominated by the creation and relaxation of carriers in the volume limited by the optical penetration depth. The upper limit of the quantum efficiency of this first step amounts to 3%. The fast rise corresponds to the creation of charge carriers and therefore is ascribed to conventional photoconductivity. The slower decay may be assigned to thermally detrapped carriers. The extreme speed of the transients in Cu salts is most probably connected with the three-dimensional (3D) charge transport. This 3D characteristic entails high percolation probability (rise) and efficient trapping (decay).

As a reference, the low-dimensional system $h_8$-Li(DCNQI)$_2$ (anisotropy $10^4$:1 [16]) was investigated. Apart from a fast component, an additional slow transient is observed (cf. bottom of Fig. 3). This second component increases and decays on the $\mu s$ scale. It reminds one of early work on K-TCNQ [17], where the thermally activated propagation of kink-type domain walls (interpreted as polarons and bipolarons) in a bond-ordered-wave lattice distortion was discussed as a possible mechanism of the conductivity. With regard to the temperature dependence of the Li salt the slow transients can be understood assuming the diffusion of heat from the surface into the volume. The peak current of 0.8 mA requires an increase of the conductivity by 2 orders of magnitude which roughly corresponds to heating by 20 K. However, the behavior of the Cu salts is completely different, stimulating the consideration of different dimensionality, charge transport, and heat diffusion in both systems.

Sample heating as well as any pressure pulse created by laser irradiation can be excluded as mechanisms of the insulator metal phase transitions in the Cu salts for the following reason: If heating or a pressure wave were the only responsible mechanisms for the phase transition, identical effects would be expected at all operating points, especially at op1 and op2, which can be chosen as close as 5 K apart (Fig. 3). Simple laser heating cannot cause a metallic conversion at op3 under the condition



FIG. 4. (a) Wavelength dependence of the transient current of $d_6$-Cu(DCNQI)$_2$ at operating point op1 ($\times$), $T = 80$ K, $E = 2 \, V \, cm^{-1}$. Enlarged ($\times 10$), the response at operating point op2 is given ($\bigcirc$), $T = 55$ K, $E = 10 \, V \, cm^{-1}$. The dotted line indicates the frequency doubled Nd:YAG laser output at $18\,750 \, cm^{-1}$ (533 nm). The inset shows the molecular structure of M(DCNQI)$_2$ where M is a metal. (b) Molecular extinction $\epsilon$ of the DCNQI$^-$ anion in CH$_3$CN solution at 300 K.

that at op2 the heating-induced transition does not occur. The linear $E$-field dependence observed in the Cu salts is in line with the high mobility $50 < \mu < 100$ cm$^2$ (V s)$^{-1}$ above op1 ($\sigma \approx 500\,000$ S cm$^{-1}$) and the high dielectric constant $\epsilon \approx 100$ [15]. These values are unusual with respect to ordinary organic photoconductors and provide efficient charge separation even in small $E$ fields. Recombination is prohibited by effective screening. The low fields applied here ($<100$ V cm$^{-1}$) also exclude dielectric breakdown as a possible mechanism. Our small $E$ fields and the absence of a threshold contrast the situation of inorganic charge-ordered states in which persistent conductivity can be conserved by fields above a given threshold [9].

At op1 and op3 photoexcitation produces delocalized carriers and the conductivity increases rapidly. In addition, this disturbs the feedback mechanism between Peierls distortion and localization of charges. We propose that due to electron lattice coupling the Peierls distortion cannot be maintained and the conducting phase is reestablished as long as the carriers are not trapped. In our model for the fast switching, the reversal of the Peierls distortion is essential, as it is accompanied by a large structural change (cf. Fig. 1). This creates a sound wave which can travel at a speed of approximately 3 $\mu$m ns$^{-1}$ (estimated from the measurement of the $E$ modulus [12]). Increasing the intensity of the photoexcitation above the threshold, the effect of irradiation can be transported into regions of the crystal which are outside the optically excited volume. From our cw experiments we conclude an optical penetration depth of 100 nm at the wavelength of 533 nm. Increasing the excitation power, larger parts of the crystal are switched into the conducting state. Because of mechanical stress between conducting and nonconducting parts of the sample, the larger conductive volume is more stable than a smaller one, and therefore the decay becomes slower. Assuming the dc conductivity of the metallic phase, the volume necessary to carry the current actually measured in experiments with strong excitation must be at least 100 times larger than the optically excited volume. This lower limit results from taking into account the series resistances which are located in our circuit. The effective quantum efficiency of the time integrated current finally yields 100 electrons/photon at 18 750 cm$^{-1}$ ($\lambda = 533$ nm at op1 and op3).

A correlation of conductivity and local charge transfer between the counterions and the DCNQI molecules is inferred by the spectral dependence of the current response to optical excitation. Starting at the Peierls distorted state which means a trimerization in the case of the Cu salts and a di- or tetramerization in the non-Cu salts, any optical excitation above the Peierls gap leads to an increase in conductivity. From the molecular point of view, anions are easiest to oxidize because of their lower ionization energy with respect to neutral species. Therefore their fingerprint in the optical spectrum is found in our experiments. The

structured absorption around 15 000 cm$^{-1}$ is a molecular feature which is present in all non-Cu salts of DCNQI. Its absence in the Cu salts is attributed to the $p\pi d$ hybridization of the DCNQI frontier orbitals with Cu $3d$ states in the conducting phase and a resulting metal-like electronic reflectivity. The temporal response to photoexcitation at different wavelengths can be understood considering the variation of the absorption discussed above. Using a constant net excitation the transients show good agreement.

In conclusion, extremely fast restoration of conductivity was accomplished by optical excitation of the Peierls distorted state. The unconventional speed of the decay in the Cu salts requires taking into account the quasi-three-dimensional charge transport of excited carriers which enables fast trapping. On the other hand, if the highly conducting state is established in a large part of the crystal, the structural nature of the transition is responsible for the extreme pertinence of the transient conductivity. Thin films now available [18] might be useful for the design of high-speed electro-optical switches in the field of solid state molecular electronics.

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