# PECULIARITIES OF THE ELECTRONIC PROPERTIES OF THE $\kappa$-PHASE STRUCTURES (BEDT-TTF)$_2$Cu(N(CN)$_2$)X with X = Cl, Br, I

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The structure of the title compounds is similar to other $\kappa$-phase struc-
tures with respect to the checkerboard-like arrangement of the ET dimers
(ET = BEDT-TTF) in the conducting planes, but different by the tilt al-
ternation of these dimers in successive planes. The resulting inequivalence of
these planes tends to destabilize the metallic state which becomes extremely
sensitive to changes in the $S$–$S$ overlaps of neighbouring ET molecules. Such
changes may result from anion substitution, lattice expansion, or also from
ordering effects of the ethylene end groups of the ET molecules. They lead
to quite different electronic properties of the three isostructural compounds.
We focus especially on the strongly pressure-dependent properties of the
Cl-compound, where a coexistence of magnetically ordered and supercon-
ducting states with rather spectacular superconducting reentrance effects is
observed.

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## 1. Introduction

A characteristic feature of the $\kappa$-phase structure of ET charge transfer salts
(ET = BEDT-TTF) is the lack of a unique stacking direction of the ET donor
molecules. Instead, they pack themselves in dimers in a checkerboard-like fashion in
the conducting plane, their long axis being tilted slightly with respect to the plane
normal. This packing seems to be preferred whenever the anions form polymer-like
chains which run along one crystallographic axis. The resulting anisotropy in the
anion planes, the anisotropy in the quasi-two-dimensional conduction band, which
results from $S$–$S$ overlaps between ET molecules in the different directions, would
be expected to be very small, on account of the checkerboard-like arrangement. The
small anisotropy, which exists, has been studied extensively e.g. in the compound
$\kappa$-ET$_2$Cu(NCS)$_2$, whose structure is monoclinic. The Fermi surface is predicted

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to consist of an open and a closed cylindrical sheet [1], and this has in fact been corroborated quantitatively by the observation of the magnetooscillatory effects [2].

About four years ago, three new $\kappa$-phases, $ET_2Cu(N(CN)_2)X$ with X = Cl, Br, I were found by the Argonne group [3]. They differ from the previously known $\kappa$-phases by the fact that the tilt of the ET molecules alternates in sign in successive layers, which leads to a doubling of the size of the unit cell and also to an orthorhombic symmetry of the structure. The inequivalence of successive ET layers destabilizes the metallic state. Indeed, although the three compounds with X = Cl, Br and I are all isostructural, they display widely different electronic properties, as can be seen from their resistivities in Fig. 1 (a to c). The Br-compound is metallic, with a resistivity anomaly at 80 K which is characteristic of $\kappa$-phases, and becomes superconducting (SC) at 11 K. The resistivity of the I-compound rises by about a factor of 400 on cooling, showing a drop again below 9.6 K. The
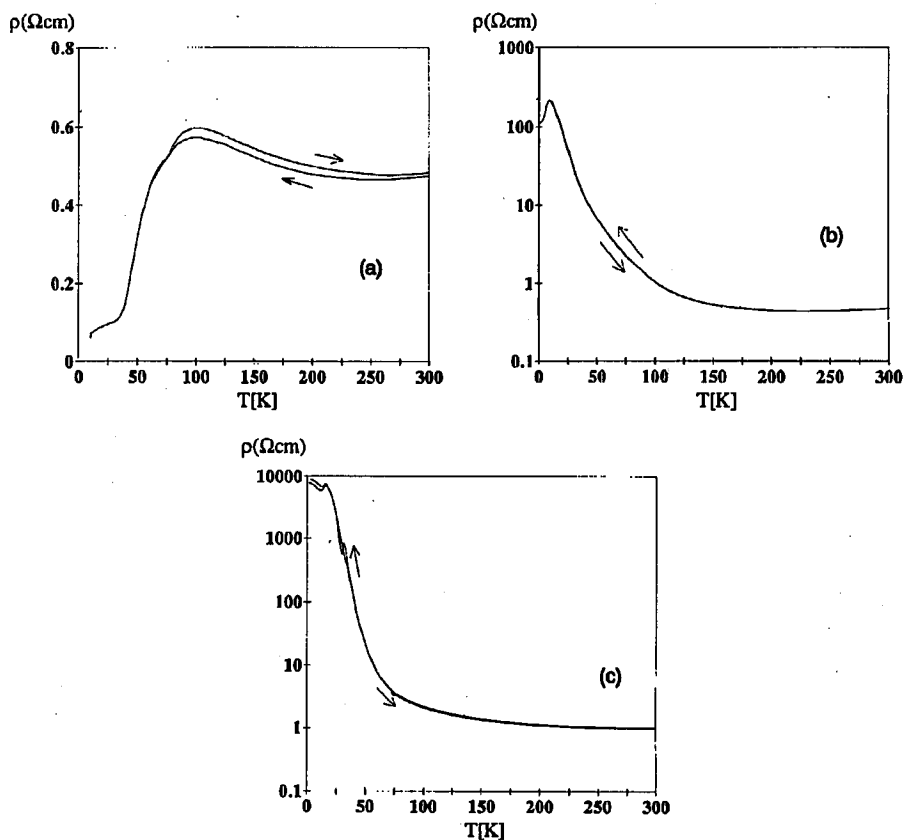


Fig. 1. Observed resistivities in the $a$–$c$ planes of the Br- (a), I- (b) and Cl-compounds (c).

Cl-compound becomes almost insulating at low temperatures, showing anomalies at temperatures where magnetic ordering phenomena have been observed or where traces of SC appear (see below). These differences suggest that the band-structure in these three compounds is extremely sensitive to small changes in the $S$–$S$ overlaps which are brought about by anion substitution, by thermal expansion effects and possibly also by order–disorder phenomena of the ethylene end groups of the ET molecules. The Cl-compound is especially interesting, since its electronic properties can be changed dramatically by the application of very moderate pressures. It has already been shown by the Argonne group that at a pressure of about 300 bar the Cl-compound, too, becomes metallic and in fact SC at 13 K, which to-date is the highest SC transition temperature in an organic compound. A detailed investigation of the resistivity versus temperature at different pressures was performed by Sushko et al. [4], who later also found the first indication of the reentrant behaviour in the SC state [5]. We have investigated in detail the magnetic and diamagnetic properties of the Cl-crystal, chiefly in order to study how the reported magnetic ordering phenomena (antiferromagnetism below 45 K and weak ferromagnetism below 22 K [6]) change as a function of pressure.

## 2. Experimental results

To do this we devised a new high pressure SQUID magnetometer made out of selected non-magnetic materials, which has a very low level of background signals. It consists of a slim Be–Cu pressure bomb, which contains the sample and in which pressures can be generated with a helium gas compressor. Care was taken in mounting the samples strain-free, with no use of grease. The bomb is located inside a slim insert cryostat which fits into a pair of SQUID detection coils kept at helium bath temperature. The temperature of the bomb can be regulated by the exchange gas pressure and by operating two heaters at its ends. The magnetic field is provided by a copper solenoid which is equipped with a movable shim coil in order to obtain a perfect balance of the SQUID detection coils. The 50 Oe maximum field of our copper solenoid is not sufficient to detect the AF (antiferromagnetic) transition which Welp et al. [6] have seen at 45 K (and which, according to the resistance anomaly in Fig. 1c may also occur at somewhat lower temperatures), but we can of course detect the weak ferromagnetic transition around 20 K. We observe a ferromagnetic remanence which always develops in the $a$–$c$ plane, the conducting plane of the crystal. Its magnitude is nearly independent of the applied field in the range below 20 Oe, and its sign is given by the sign of the applied field, however small this field is. It is probable that the remanence arises from a slight canting of an antiferromagnetic spin structure. In Fig. 2 we show how this ferromagnetic transition shifts to lower temperatures as a function of pressure, the magnitude of the remanence thereby getting smaller. Before it disappears altogether, SC appears (at 300 bar), and the first signs of the SC reentrance phenomenon can already be seen. At slightly higher pressure (310 bar), SC develops fully, but is stable only in the finite temperature interval between $T_{c1}$ and $T_{c2}$, the reentrance temperature (Fig. 3). Sweeping through the temperature $T_{c2}$ must alter the magnetically ordered state of the crystal, as shown by curve 3 of Fig. 3. The weak ferromagnetic order, which still suppresses SC (curve 2) is "switched off" in curve 3. That the
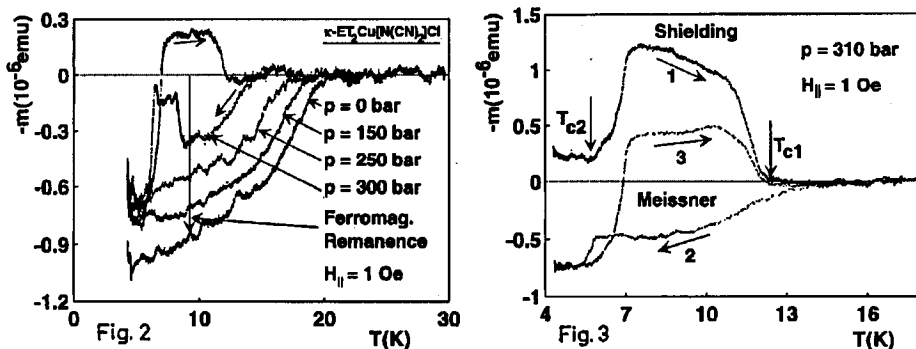
Fig. 2. Change of the weak ferromagnetic order with pressure and appearance of SC.
Fig. 3. Near complete SC reentrance at 310 bar (see text).

reentrant transition has to do with the emergence of another form of magnetic order is shown in a small and presumably near perfect crystal, which shows a complete reentrant transition, i.e. with no traceof SC in the reentrant state below $T_{c2}$ (Fig. 4). Switching on and off 50 Oe in the reentrant state again results in a small magnetic remanence, which on warming in zero field disappears at $T_{c2}$. This proves that the reentrant state, too, is a magnetically ordered state.
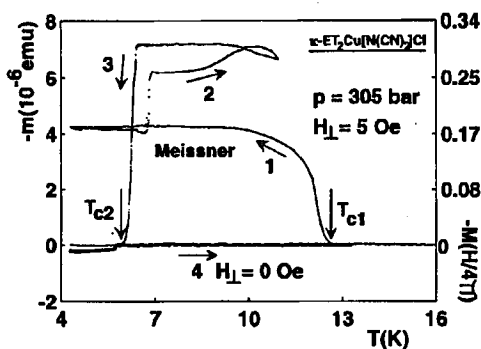


Fig. 4. Observed complete SC reentrance in a Cl-crystal.

Another important observation is the fact that the reentrant transition is correlated with latent heat, i.e. that it must be of first order. Often, on cooling, this heat emerges not only continuously but also in successive bursts which lead to a momentary warm-up of the whole pressure bomb. To investigate this effect, we built an especially small pressure bomb out of Be metal, which has a small specific heat in the helium temperature range. A result is shown in Fig. 5. The burst of heat visibly heats up the bomb and also temporarily stabilizes the SC state. One has to cool to lower temperatures to complete the reentrant transition. There is thus no doubt that this transition is of first order. This explains a lot of hysteresis effects that we have observed. The reentrant transition can easily be
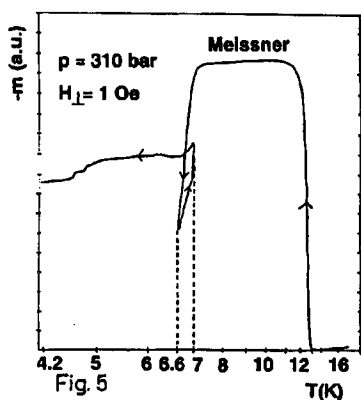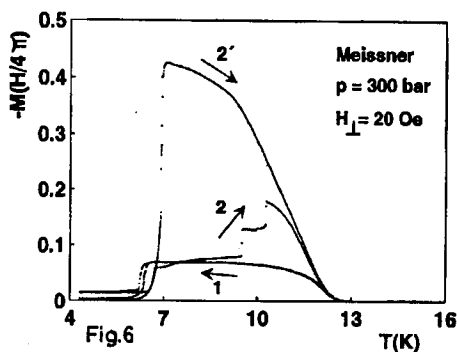
Fig. 5. Effect of latent heat during the reentrant transition (see text).

Fig. 6. Meissner signals on *warming* into the SC state at different sweep speeds: 2 — 0.1 K/min, 2' — 0.5 K/min.

supercooled by sweeping fast enough through it (see e.g. curve 1 of Fig. 4). Also, when the sample, after slow cooling, is warmed back through the $T_{c2}$ transition in an applied field, the ensuing Meissner effect again depends on both the temperature sweep speed and also on the magnetic field. Largest Meissner signals of over 40% of the shielding signal have been observed (Fig. 6).

At higher pressures ($p > 400$ bar), reentrance is no longer observed. However, we cannot rule out that we simply supercool the transition and that the stable ground state could still be the magnetically ordered reentrant state. An indication that this might be the case is shown by experiments in high magnetic fields by Sushko et al. [7]. In field above 4 T, SC is quenched completely. The reentrant state becomes a high resistance state (Fig. 7). A drop in resistivity at $T_{c2}$ shows that a phase transition is taking place, indicating that the reentrant state can be stabilized in high fields (even at higher pressures) and that, again, it must be a magnetically ordered state with a structure change at $T_{c2}$.
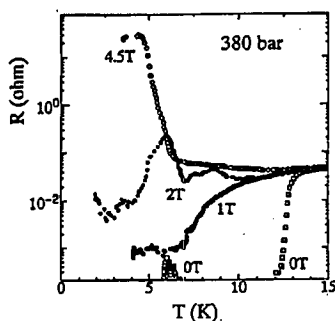


Fig. 7. Transition at $T_{c2}$ in overcritical magnetic fields (from Ref. [7]).

## 3. Conclusions

It should be pointed out that $\kappa$-ET$_2$Cu(N(CN)$_2$)Cl under pressure is the first reentrant SC without rare-earth ions. Since Cu is in the monovalent state, the magnetic ordering phenomena, superconductivity and the reentrant behaviour must arise from one and the same electron system, namely $\pi$-electrons in the ET layers. Both magnetic order and SC ultimately arise from interactions among the $\pi$-electrons and from interactions with the lattice potential. There is a possibility that the competition between magnetic order and SC may be linked with some form of intrinsic disorder in the crystal. Evidence for this is the notorious absence (so far) of magnetooscillatory effects in the metallic states of these $\kappa$-phases [8]. Other possible evidence are thermal expansion anomalies around 80 K [9] which we believe may be caused by order–disorder effects of the ethylene end groups of the ET molecules. Some features of the Cl-compound are reminiscent of the anion orientational order effects in TMTSF$_2$ClO$_4$, which can either stabilize a SC ground state (for complete order) or a high resistance spin density wave ground state (for complete disorder).

In the Cl-compound, it seems that SC is compatible with an AF state, but not with the ferri- or ferromagnetic states that we observe, and which we believe come about by a disturbance of the AF state. This disturbance must be due to subtle structure changes which remove the exact inversion symmetry of the crystal and which have not been clearly identified yet. Our observation that the $T_{c2}$-transition is of first order in fact suggests that it, too, is connected with a structure change. The unusual thing is that this happens at such a low temperature, but then again it happens only in a narrow pressure interval, where apparently the free energies of the magnetic reentrant and the SC (and possibly AF) states are nearly degenerate.

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