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PRESSURE - TEMPERATURE PHASE DIAGRAM OF (DMDCNQI)₂Ag:
A COMPARATIVE STUDY WITH RELATED COMPOUNDS

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ABSTRACT

The pressure-temperature phase diagram of the silver salt of the 2,5- dimethyl-
cicyanoquinonediimine, (DMDCNQI)₂Ag, is established by electrical resistivity measurements. In
it are included the temperatures of resistivity minima (T_p) and of the transition defined by the
anomaly in the logarithmic derivative of the resistivity. Correlating the present data with the
information from X-ray diffuse scattering and magnetic susceptibility, it is concluded that the low
temperature insulating state has a spin-Peierls character. Other important feature of this material is a
transition towards a more conductive state upon applying pressure of 10.4 kbar, at ambient
temperature. The distinct behaviour of (DMDCNQI)₂Ag (abbreviated DM-Ag) relative to the Cu
analog (DM-Cu) and (CIM-DCNQI)₂Cu (CM-Cu) is also discussed.

INTRODUCTION

A great deal of interest has been recently thrown upon the salts of the disubstituted dicyano-
quinonediimine (DCNQI) radical anion, specially because of the metallic conductivity of DM-Cu
down to 0.45 K[1]. Contrarily to all expectations based on the behaviour of organic conductors so
far studied under pressure, in this compound the application of pressure induces a metal-insulator
transition[2,3], and the phase diagram exhibits the feature of a re-entrant metallic phase at very
moderate pressure[3]. It has been suggested that the copper ion plays a role in this compound,
acting as a bridge between the organic stacks[1] and experimental evidence has been provided of a
mixed-valence state of $\sim +1.3$ for the Cu ion either in this compound and in CM-Cu[4].

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We have performed a pressure study of DM-Ag, where a mixed-valence state is very unlikely to occur due to a high energy barrier between the +1 and +2 valence states of silver. The details of that study are presented elsewhere[6]. Here, we show a comparison between the phase diagram of DM-Ag and those of the copper salts of DMDCNQI and CIMDCNQI.

The three compounds are isostructural, belonging to the tetragonal system, space group $I4_1/a$ [5]. An X-ray diffuse scattering study showed that the Ag compound exhibits both $4k_F$ and $2k_F$ one-dimensional instabilities, condensing into satellites at 100 and 83K respectively[7]. CIM-Cu has a structural transition at 210K, where a three-fold periodicity along the stacking direction is accomplished[4], which does not present any 1-D precursor effects[8].

RESULTS

The normalized conductivity as a function of applied pressure, at room temperature, has a different behaviour for DM-Ag on one side and for the two copper salts on the other side (Fig.1). For the Ag compound, the conductivity increases always with increasing pressure, whereas for the CIM and DM copper salts, it passes through a maximum and at pressures in excess of 2 and 9 kbar respectively, it is already lower than the normal pressure value. In DM-Ag, a step is noticeable centered at $P_S=10.4$ kbar. Below that anomaly, the increase of the conductivity is $12.5\% \text{ kbar}^{-1}$ and above $23\% \text{ kbar}^{-1}$, with an overall value of ca. $30\% \text{ kbar}^{-1}$.

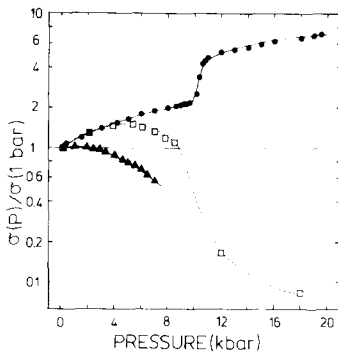


Fig. 1. The normalised conductivity $\sigma(P)/\sigma(1 \text{ bar})$ as a function of pressure for $(\text{DMDCNQI})_2\text{Ag}$ (closed circles), $(\text{DMDCNQI})_2\text{Cu}$ (open squares) and $(\text{CIM-DCNQI})_2\text{Cu}$ (closed triangles). Notice the logarithmic scale for the normalised conductivity. The solid and broken lines are merely eyeguides.

The plots of the resistivity/temperature runs for DM-Ag are displayed in Fig.2, for several values of the pressure. At 1 bar, a shallow minimum is observed at $\approx 170\text{K}$ and below it, the resistivity increases gradually, the slope of $\ln\rho$ versus $1/T$ becoming constant for $T \leq 80\text{K}$, without any sign of an anomaly in the derivative $d(\ln\rho)/d(1/T)$. However for $T \geq 4$ kbar, such anomaly is noticeable and the transition becomes sharper with increasing pressure up to 7.5 kbar. For

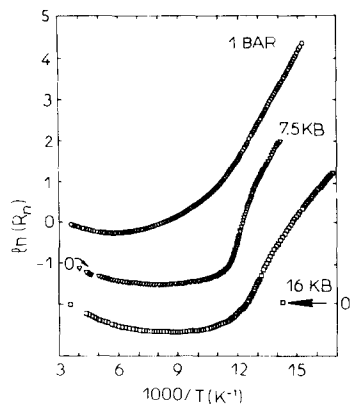


Fig.2. The normalised resistivity versus reciprocal temperature plots for $(\text{DMDCNQI})_2\text{Ag}$: 1 bar (circles); 7.5 kbar (triangles) and 16 kbar (squares). The left hand logarithmic scale is valid for 1 bar, and resistivity was normalised to the R.T. value of $10^{-2} \Omega\cdot\text{cm}$.

pressures higher than P_S , the pressure of the conductivity step at R.T., that anomaly is still present but is not sharper than at 7.5 kbar. The temperature of the resistivity minimum decreases with increasing pressure, whereas the transition temperature is much less sensitive to pressure, showing only a slight tendency to increase that seems to have a discontinuity at P_S (Fig.3).

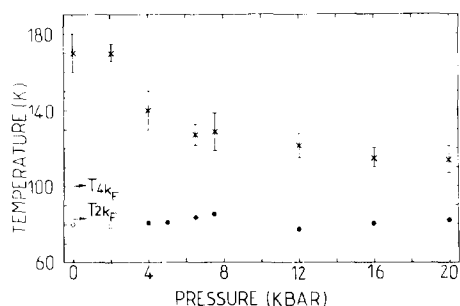


Fig.3. The phase diagram of $(\text{DMDCNQI})_2\text{Ag}$. Crosses represent the temperature of resistivity minimum (T_0), closed circles represent the transition temperature, defined by the anomaly in the derivative $d(\ln\rho)/d(1/T)$ and the open circles that of the highest temperature for which that slope remains constant. The arrows on the left side represent the temperatures of condensation of $4k_F$ and $2k_F$ satellites at 1 bar, after ref.7.

The described behaviour contrasts with that of DM-Cu and CM-Cu. The behaviour of the latter compound can be scaled to that of DM, shifting its phase diagram along the P axis of ≈ 5 kbar, except that only one transition is observed in all the pressure range (Fig.4). The thermoelectric power shows also an important difference between DM-Ag and its copper analog (Fig.5). Our results for DM-Cu agree with those obtained by Mori *et al.*[9]. The absolute value for the Ag salt increases smoothly down to $\approx 120\text{K}$ and drops at $\approx 80\text{K}$. On the contrary, in the high temperature range, the thermopower of DM-Cu exhibits a metal-like behaviour but, as temperature decreases, deviations from linearity become more pronounced and a peak occurs at $\approx 40\text{K}$.

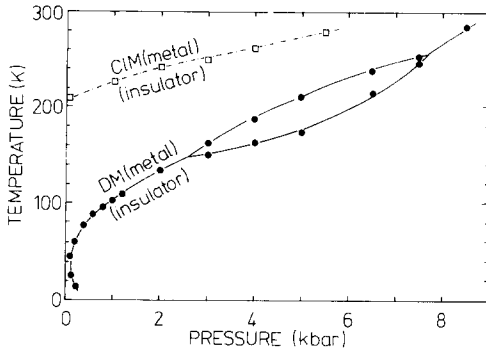


Fig.4. The phase diagram of $(\text{CIM-DCNQI})_2\text{Cu}$ compared to that of $(\text{DMDCNQI})_2\text{Cu}$. The first can be superposed to the second, by a shift along the P axis of ca. 5 kbar.

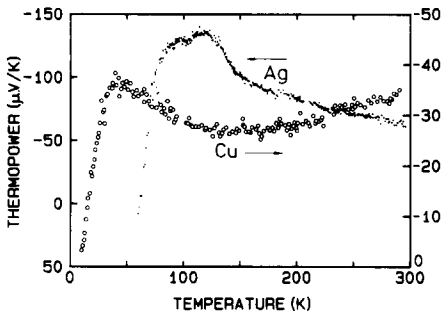


Fig. 5. The thermoelectric power of $(\text{DMDCNQI})_2\text{Ag}$ and $(\text{DMDCNQI})_2\text{Cu}$.

DISCUSSION

The one-dimensional character of DM-Ag was clearly evidenced by Moret *et al.*[7] through X-ray diffuse scattering experiments. The $4k_F$ diffuse sheets, visible even at R.T., condense into satellites at 100K (dimerisation) and upon cooling, the $2k_F$ diffusion appears, condensing itself at 83K (tetramerisation). At the temperature of the $4k_F$ condensation T_{4k_F} , the resistivity profile at 1 bar does not exhibit any anomaly. On the other hand, the T_{2k_F} agrees with the drop in the ESR signal intensity, which is independent of crystal orientation[10,11]. At this temperature (83K), the charge degrees of freedom are already frozen and the resistivity is five times its minimum, $\rho=5\rho_m$. As the $2k_F$ condensation involves the loss of the spin degrees of freedom, this transition has a spin-Peierls character.

The behaviour of the present compound recalls some of the features of other two spin-Peierls systems: $\text{MEM}(\text{TCNQ})_2$ and $(\text{TMTTF})_2\text{PF}_6$. It undergoes both the $4k_F$ and $2k_F$ structural transitions like in first compound[12,13] and as in the second, it exhibits a resistivity minimum that is not connected with a structural transition and a thermopower that approaches a semiconductive

behaviour[24] even when the resistivity has the metal-like behaviour for $T > T_p$. However, DM-Ag differs markedly from both SP systems. In $\text{MEM}(\text{TCNQ})_2$, the $4k_F$ transition (335K) is assigned to regular Peierls transition in a "big U" ($U/4t \rightarrow \infty$) system[13], so in an effectively half-filled band, with the opening of a gap at the Fermi level. In $(\text{TMTTF})_2\text{PF}_6$, the dimerisation exists already at room temperature as shown by structural studies [14,15], and so the band is also half-filled. The resistivity minimum has been explained as arising from electron-electron Umklapp scattering processes which are relevant for that band-filling[16,17]. The spin-Peierls transition occurs at 19K[18] with 1-D precursor effects visible from 60K[19]. In DM-Ag, the temperature range of dimerisation is very narrow ($\approx 20\text{K}$) and T_p occurs when the dimerisation is only fluctuative.

The coulombic correlations are known to play an important role in 1-D systems, and in the present compound there is also experimental evidence for them, by the magnetic susceptibility enhancement relative to the Pauli value[11]. However, such enhancement is not so large as for $\text{MEM}(\text{TCNQ})_2$ [13] and the temperature dependence of the magnetic susceptibility is different for both compounds. We believe that for DM-Ag the coulombic correlations must be of intermediate strength and that its behaviour can be understood weighting the models for $U=0$ and $U=\infty$.

The phase diagram evidences also the differences from $(\text{TMTTF})_2\text{PF}_6$. Whereas for the latter, the applied pressure shifts both T_p and the transition in the resistivity to lower temperature[20], for DM-Ag, it makes a transition to be noticeable by resistivity measurements. This transition is probably of the Peierls type. In fact, as it has been recently shown, it is possible to evolve continuously from a Peierls to a spin-Peierls transition[17,21]. Our compound at 1 bar is probably not far from the loose borderline between the two states. As it was shown for the $(\text{TMTTF})_2X$ family, the ground state can change by application of pressure, or be different from one member of the family to other, due to subtle changes in the Hubbard gap, the dimerisation gap or the electron-phonon coupling constant[17]. Experimentally, it has been proved that the spin-Peierls transition in $X=\text{PF}_6$ at 1 bar, becomes SDW under a pressure of 12 kbar[22]. The decrease of T_p with pressure (Fig.4) is an indication that the Hubbard gap changes, possibly enough to make the transition of the Peierls type. For instance, it has been shown in $\text{MEM}(\text{TCNQ})_2$ that pressure tends to merge the spin-Peierls ($2k_F$) and the Peierls transition ($4k_F$) into a unique one[23].

The validity of our hypothesis can only be tested through structural studies under pressure, which are also required for the understanding of the nature of the conductivity vs. pressure anomaly at R.T. in DM-Ag or the mechanism of the pressure-induced transitions observed in DM-Cu. For this compound, it has been argued that a probable effect of pressure is to decrease the copper oxidation and the interstack coupling, making the conductor more one-dimensional[3]. However, CM-Cu at 1 bar seems to correspond to DM-Cu under 5 kbar or so. It does not exhibit any 1-D precursor effects of its transition [8] and the periodicity of the distorted lattice is in good agreement with the mixed valence of 1.3 for Cu, thus not supporting the hypothesis previously made, what is discussed elsewhere in this Conference.

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