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LETTER TO THE EDITOR

The pressure–temperature phase diagram of the organic conductor (2,5 DM-DCNQI)₂Cu

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Abstract. We show that it is possible to suppress the ambient-pressure metallic phase in (2,5 DM-DCNQI)₂Cu by applying a pressure—even one as low as 100 bar. On increasing the pressure up to 8.5 kbar, the metal–insulator transition temperature increases and its strong first-order character becomes weaker, whereas the activation energy stays constant. In addition, a re-entrance of the metallic phase is observed at very low temperatures up to pressures of about 300 bar.

Recently, a new class of quasi-one-dimensional organic compounds (2,5 DM-DCNQI)₂X, where X is an inorganic cation, has attracted much interest (Aumüller *et al* 1986, von Schütz *et al* 1986). These materials are single-chain organic conductors where the 2:1 stoichiometry and the +1 oxidation state for cations such as Li, Na, K, Ag lead to a quarter-filled conduction band formation by the overlap of $p\pi$ DM-DCNQI orbitals on the organic chains. Furthermore, the one-dimensional nature of these compounds is quite important, leading to metal–insulator transitions at low temperatures (Kato *et al* 1987, Werner *et al* 1988).

However, (2,5 DM-DCNQI)₂Cu stands apart from all the others because of an intermediate valence state of the copper ions between +1 and +2 (Schmeisser 1987, Kobayashi *et al* 1987). At ambient pressure, this compound displays metallic behaviour down to 450 mK, without there being any sign of a superconducting ground state.

We have already reported (Tomić *et al* 1988) measurements of the electrical conductivity under pressure; these revealed the onset of an insulating phase at a transition temperature varying from 70 to 286 K for pressures between 300 bar and 8.5 kbar. Moreover, two relatively smooth phase transitions were observed at pressures above 3.5 kbar, while only one—but extremely sharp—phase transition was noticed at lower pressures. However, some particular properties of the intermediate- and the low-pressure regions, like (i) the apparent coexistence of two smooth and one sharp phase transition on warming and cooling, respectively, in the former and (ii) the constant

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transition temperature in the latter, required more attention. In particular, we had noticed that the pressure technique in which isopentane is used as a pressure-transmitting medium was not appropriate for working at low temperatures in the low-pressure regime ($p \approx 5$ kbar) because of the substantial drop of pressure occurring upon cooling.

Therefore, we have undertaken a new investigation of the phase diagram of $(2,5 \text{ DM-DCNQI})_2\text{Cu}$ using the helium gas pressure technique up to 7.5 kbar, with a particular emphasis on the low-pressure region ($p < 1$ kbar). The present study confirms the main qualitative features of the phase diagram at high pressures and also shows that the determination of the pressure at low temperatures in the low-pressure region ($p < 5$ kbar) in our previous publication was somewhat erroneous. Hereafter, we present a complete phase diagram determined entirely by the helium gas pressure technique (apart from the point at $p = 8.5$ kbar) with a control of the pressure that amounts to about ± 20 bar.

In this work, we have used six different single crystals of typical dimensions $2 \text{ mm} \times 2 \times 10^{-4} \text{ mm}^2$. In particular, all measurements up to 2 kbar were performed on one high-quality single crystal and verified to be perfectly reproducible on two others.

The temperature–pressure (T – p) phase diagram is shown in figure 1. A metallic phase that exists down to very low temperatures at ambient pressure becomes unstable against an insulating phase above 100 bar. The transition into the insulating phase is strongly first-order as the resistance jump is of the order of 10^4 at least. On increasing the pressure, the magnitude of the resistance jump decreases and the transition temperature increases. At $p = 2$ kbar the estimated activation energy (Δ) is about 1300 K which gives for the ratio $2\Delta/T_c$ the very large value of 19. Increasing the pressure to above $p = 2$ kbar induces a splitting of the transition line into two branches. This splitting is maximal around 5 kbar. Above this pressure the two transition lines get closer to one another and finally merge into a single branch above 7.5 kbar.

The plot of the logarithm of the normalised resistance versus the inverse of temperature for pressures between 2 and 7.5 kbar is displayed in figure 2. Note that despite the appreciable rise in transition temperature, the magnitude of the activation energy does not depend much on the applied pressure. Consequently, the ratio $2\Delta/T_c$ diminishes, reaching a value of about 10 for $p = 7.5$ kbar.

We turn now to the description of the low-temperature behaviour of $(2,5 \text{ DM-DCNQI})_2\text{Cu}$ at pressures lower than $p = 1$ kbar. The evolution of the phase transition

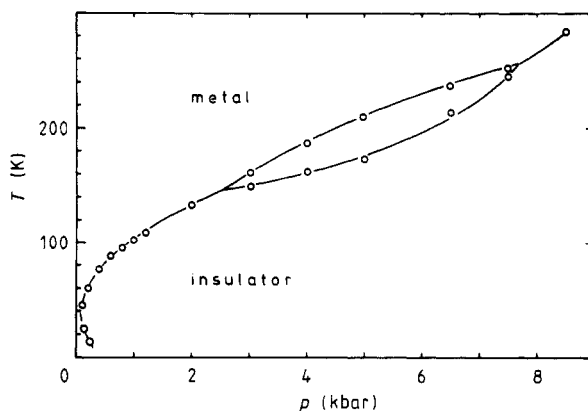


Figure 1. The temperature–pressure phase diagram of $(2,5 \text{ DM-DCNQI})_2\text{Cu}$.

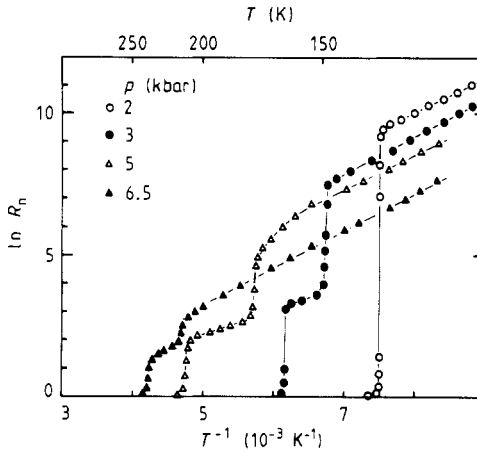


Figure 2. The logarithm of the normalised resistance versus the inverse of temperature as a function of pressure.

towards the insulating phase as a function of pressure is shown in figure 3. As we mentioned before, the extremely sharp transition persists down to 100 bar (for $p = 110$ bar, $T_c = 47$ K). In order to check the stability of the low-temperature phases, we have used two distinct approaches. Firstly, we have chosen a particular pressure and have varied the temperature, and secondly we have cycled the pressure keeping the temperature constant. In this way, we have observed a very interesting low-pressure T - p phase diagram, which is displayed in figure 4. The most extraordinary property is certainly the restabilisation of a metallic phase at low temperatures above 100 bar. In what follows, we will describe two typical T - (and p -) cyclings, which have led to the final presentation of the phase diagram in figure 4.

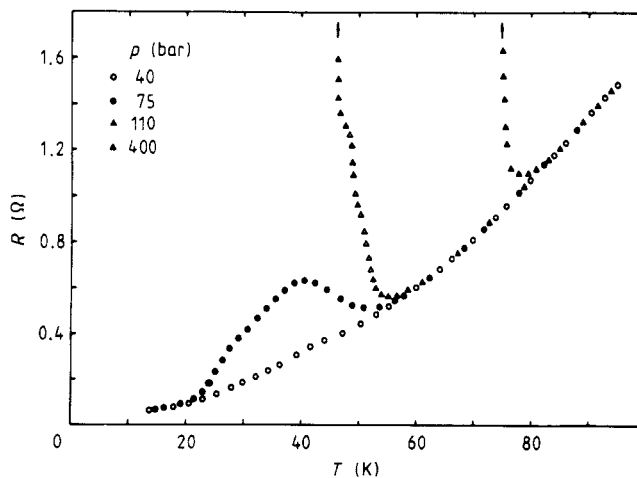


Figure 3. Resistance versus temperature in the low-pressure region.

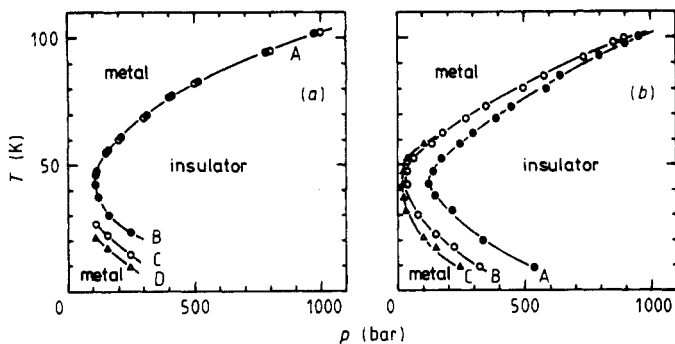


Figure 4. The low-pressure phase diagram of $(2,5 \text{ DM-DCNOI})_2\text{Cu}$. (a) p fixed, T variable. Open and full circles: cooling and warming, respectively; open triangles: the first cooling only. (b) T fixed, p variable. Open and full circles: decreasing and increasing pressure, respectively; open triangles: the first pressure decrease.

In figure 4(a) the pressure is fixed at high temperatures.

(i) On cooling down, the material leaves the region of the metallic phase at curve A (open circles) and remains insulating down to the transition line marked by the open triangles (curve D) and open circles (curve C) for the first and subsequent coolings from the insulating phase, respectively. Below these curves, the material re-enters the metallic region.

(ii) On warming, the material stays metallic up to curve B (full circles), above which it enters the insulating region and leaves it again at curve A (full circles).

The behaviour of the sample at $p = 150$ bar is shown in figure 5. Note that the broken curve relating the high- and the low-temperature region exactly represents the resistance behaviour of the material at a pressure of 40 bar (figure 3).

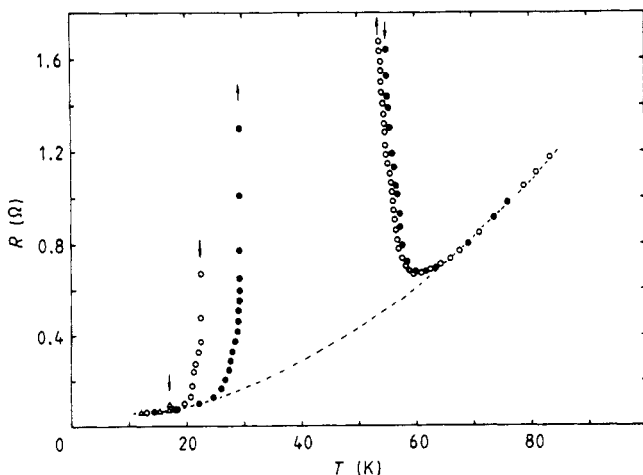


Figure 5. Resistance versus temperature at $p = 150$ bar. Open and full symbols: cooling and warming respectively (see figure 4 and the text).

In figure 4(b), the temperature is fixed below 60 K in the insulating phase.

(i) On releasing the pressure, the material leaves the insulating phase by crossing the third (open triangles) and the second (open circles) curves on its first and subsequent departures, respectively.

(ii) On increasing the pressure, the material stays metallic until the first line (full circles) is crossed, where it enters the insulating phase.

We can summarise the main results as follows. A very low pressure of 100 bar is sufficient to induce a phase transition from a metallic ambient-pressure phase to an insulating phase at low temperatures. However, a metallic phase is established as the ground state at very low temperatures up to pressures of about 300 bar. Moreover, considering that under 150 bar (figure 5) the temperature dependence of the conductivity is similar above and below the small temperature region where the compound becomes an insulator, we may infer that the conducting ground state is of the same nature as the conducting state at high temperatures. It is also worth noting the existence of strong hysteretic behaviour when the material is cycled between the insulating and metallic phase at low temperatures. Furthermore, as the pressure increases from 100 bar to 8.5 kbar, the transition temperature gets higher and the first-order character becomes weaker whereas the activation energy stays constant. Between about 2.5 and 7.5 kbar, the crossing from the metallic to the insulating phase proceeds in two steps (figure 2). Their temperature separation increases up to 5 kbar and then decreases again so as to merge above about 7.5 kbar.

In conclusion, the present high-pressure study of the organic conductor $(2,5 \text{ DM-DCNQI})_2\text{Cu}$ has revealed a pressure-temperature phase diagram that is somewhat unusual for a low-dimensional conductor. The mixed valence of copper cations in this material is likely to promote an easy transfer of carriers between the stacks of organic anions. Therefore, a possible effect of pressure is to decrease the copper oxidation state and the inter-stack coupling concomitantly. Thus, at high pressure, the conductor becomes more one-dimensional and the transition towards the insulating state occurs at high temperatures. Moreover, the re-entrance that is observed in the low-pressure region of the phase diagram may be attributed to thermal expansion effects balancing the influence of pressure.

Finally, more experiments involving, e.g., x-rays and NMR under pressure would be most rewarding as regards obtaining an understanding of this new one-dimensional compound.

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