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Pressure-Induced Neutral-Ionic Phase Transition in the Mixed-Stack 2:1 Charge-Transfer Complex (EDT-TTF-I_2)$_2$TCNQF

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Abstract

We explored the neutral-ionic phase transition in (EDT-TTF-I_2)$_2$TCNQF by measuring the electrical conductivity as a function of temperature and hydrostatic pressure (up to 11.8 kbar). At about 4.3 kbar the compound undergoes the transition to quasi-ionic phase at the temperature about 100 K; the transition temperature increases as the pressure grows. We propose a pressure-temperature phase diagram, discussed in comparison to analogous data obtained for mixed-stack 1:1 charge-transfer complexes which also undergo a neutral-ionic transition. We suggest that the transition smearing can be related with the fact that in this 2:1 complex, not only the Madelung energy but also the ionization potential of donors grow as the crystal lattice contracts on temperature decreasing.

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Introduction

Temperature-induced neutral-ionic (N-I) transition is a very rare phenomenon, observed in organic 1:1 charge-transfer (CT) complexes composed of alternating π-electron donor (D) and π-electron acceptor (A) molecules arranged in mixed one-dimensional stacks (...DADADA…). Uniqueness of this phenomenon is that in the simplified picture a single material undergoes transition between van der Waals molecular crystal (neutral phase) and ionic crystal (ionic phase). Abrupt or continuous change of the degree of CT between molecules (ρ), is observed when the difference between the ionization energy of donor (I_D) and the electron affinity of acceptor (E_A) becomes comparable with the increment of electrostatic Madelung energy (M) of the ionized lattice, induced by thermal contraction of the crystal ($I_D - E_A \sim M$). The application of hydrostatic pressure also yields a lattice contraction and modifies intermolecular interactions and thus Madelung energy; therefore the N-I transition can be also induced by pressure. The change of ρ is usually accompanied by dimerization of the regular mixed-stack chains, therefore the phase transition is to be considered as both N-I transition and Peierls distortion. Because of sizable interactions between frontier orbitals in the DA stacks, the neutral (ρ=0) and ionic (ρ=1e) configurations are always mixed to some extent. Consequently, in real crystals the N-I transition rather takes place between quasi-neutral (ρ<0.5e) and quasi-ionic (ρ>0.5e) ground states[1-5].

The first example of the N-I transition was reported in the 1:1 complex formed by the donor tetrathiafulvalene (TTF) and the acceptor chloranil (CA), and this complex was the most thoroughly and widely studied and serves as the prototype of this ordering phenomenon[1-4,6,7]. On temperature decreasing, at T=81 K the TTF-CA crystal shows an abrupt transition from the quasi-neutral (ρ=0.3e) to quasi-ionic (ρ=0.6e) phase. The ionicity change is accompanied by a dimerization of the mixed stacks and appearance of electronic ferroelectricity or antiferroelectricity of the complex[6,7]. Moreover, the N-I transition in TTF-CA can be also realized by pressure[8-11] or light[12-14] too. The temperature-induced N-I transition was also discovered in some other organic CT complexes of 1:1 stoichiometry with mixed stacks under ambient or moderate pressures[3,4]. There are also reports about the N-I transition at very high pressures (p>2GPa) in a few 2:1 complexes with a local DAD trimer structure[15,16] but these studies were not followed up in more detail. Since the most distinct N-I transitions were

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observed in 1:1 complexes, the vast majority of the investigations were performed for these molecular systems.

The N-I transitions in molecular DA complexes were studied using a variety of experimental techniques. Very powerful methods are IR and Raman spectroscopies since some intra-molecular vibrations are strongly charge sensitive; in a good approximation their frequency depends linearly on charge density *(ρ)* on molecules[2,10,11,15-17]. The ρ estimated from vibrational spectra is more accurate than that one determined from crystallographic data and agree very well with NMR data. The N-I transition induced by both pressure and temperature can be also observed with the help of electrical conductivity methods – this technique clearly shows modifications of both ionicity and crystal lattice that are usually detected as resistivity anomalies[4,9,18,19]. Because of the mixed-stack structure the crystals exhibit semiconducting properties. A characteristic feature is that the activation energy of conductivity estimated from Arrhenius plot (usually smaller than 0.15 eV) is much less than the optical energy gap (about 0.5 eV). This observation gives evidence that lower-energy excitations are responsible for the conductivity. These excitations were identified as N-I domain walls in the neutral phase[20,21] and spin solitons in the ionic phase[20,22].

Recently, a temperature-induced N-I conversion was discovered in the mixed-stack complex (EDT-TTF-I_2)$_2$TCNQF (where EDT-TTF-I_2 is diiodoethylenedithio-tetrathiafulvalene and TCNQF is monofluoro-tetracyano-p-quinodimethane)[23,24]. To the best of our knowledge, this is the first observation of such effect in a 2:1 complex under ambient pressure. The compound crystallizes in the triclinic system (space group $P\bar{1}$) with one TCNQF acceptor on inversion center and one EDT-TTF-I_2 donor in general position in the unit cell, hence the 2:1 D_2A stoichiometry. The molecules are arranged in mixed stacks …ADDADDA… and the parallel stacks interact to each other to form layers. The neighboring layers are connected by highly directional C–I···N≡C halogen bonds. Both crystallographic and spectroscopic (IR and Raman) studies showed that the degree of CT (ρ) between donors and acceptor is continuously increasing from about zero at room temperature to about 1*e* at T = 8 K (with a regime change at about 100 K), i.e. the complex undergoes a N-I conversion. It is remarkable that the spectroscopic data indicate that ferroelectric domains, created in stacks by the N-I transition, fluctuate between

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opposite directions[24]. It was suggested that such effect should be common for the 2:1 mixed-stack complexes.

Here, we present DC electrical conductivity measurements of (EDT-TTF-I_2)$_2$TCNQF single crystals as a function of both hydrostatic pressure and temperature. Our goal is to investigate the N-I transformation in this mixed stack 2:1 complex. We show that the enhancement of ρ has an influence on the crystal conductivity. Our results will be discussed in comparison with analogous data obtained for 1:1 complexes.

Experimental Section

Single crystals of (EDT-TTF-I_2)$_2$TCNQF were prepared following the procedure described previously[23]. The DC resistance in the direction of stacking axis was measured by the four-probe method at ambient pressure and by the two-probe method at high hydrostatic pressures. The electrodes were prepared with a gold paste. In order to measure the electrical resistivity under pressure we used a clamp-type cupper beryllium cell and Daphne 7373 oil as a pressure transmitting medium. After clamping the cell at a selected pressure (up to 11.8 kbar) at room temperature the sample resistivity was measured as a function of temperature. Due to thermal contraction the actual pressure is significantly reduced (ca. 1.5 kbar) on temperature decreasing down to 10 K, therefore suitable pressure corrections were done taking into account the data for Daphne 7373 oil[25,26,27,28]. We estimate that after corrections the real pressure at low temperatures is known within an accuracy ± 0.5 kbar. For each mounted sample all the pressure and temperature measurements were performed without opening the pressure cell.

Results

The room-temperature electrical resistivity of (EDT-TTF-I_2)$_2$TCNQF at ambient pressure (p=0) is rather high (about 5 $\times 10^3$ Ωcm), which is typical for mixed stack complexes in the neutral phase. Temperature dependence of the resistivity is displayed in Fig. 1. At 100 K and 90 K the resistivity shows small and sharp jumps (they are better seen in Fig. 2). Analogous kink-like resistivity anomalies were also observed for other complexes and correlated with N-I transition. In the case of TTF-CA the kink is about one order of magnitude and occurs at the N-I transition temperature[9] but in the case of (EDT-TTF-I_2)$_2$TCNQF both kinks are much smaller. The kink at 100 K well corresponds with the temperature of regime change indicated by IR and

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Raman data[24]. Evidently, at 100 K and 90 K the crystal undergoes an abrupt but small modification which can be related to a weak change of ionicity and/or deformation of the crystal lattice. Modifications of intermolecular interactions (e.g. halogen bond interaction) should be also taken into account. On closer examination one can also distinguish three other smaller resistivity anomalies at temperatures 96, 92 and 91 K (see Fig. 2). The resistivity reduction seen at the lowest temperatures in Fig. 1 is an artifact due to limits of the sensitivity of our apparatus. No thermal hysteresis was observed on temperature cycling (see Fig. S1 – Supplementary Material). The ambient pressure resistivity data show that the complex is a semiconductor with two activation energies: 109 and 86 meV above and below 200 K, respectively. In our previous studies for crystals from other batches, these energies were determined as equal to 108 and 72 meV, respectively[23].

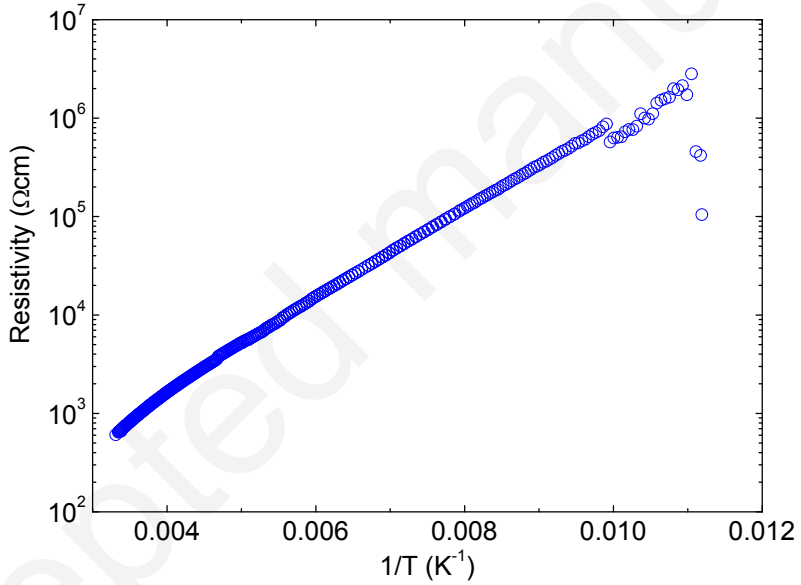


Fig. 1. Temperature dependence of the electrical resistivity of (EDT-TTF-I_2)$_2$TCNQF determined by the four-probe method at ambient pressure (p=0).

Temperature dependence of the crystal resistivity under various pressures is displayed in Fig. 2. The application of pressure strongly decreases the resistivity. It should be noted that the pressure applied at room temperature, indicated in the right part of the figure, is reduced on temperature lowering due to thermal contraction of the pressure medium. Nevertheless, in Fig. 2 we show original results, without any suitable corrections of pressure which should be done for lower temperatures. These data are analogous to those reported for the 1:1 complexes[9,18,19].

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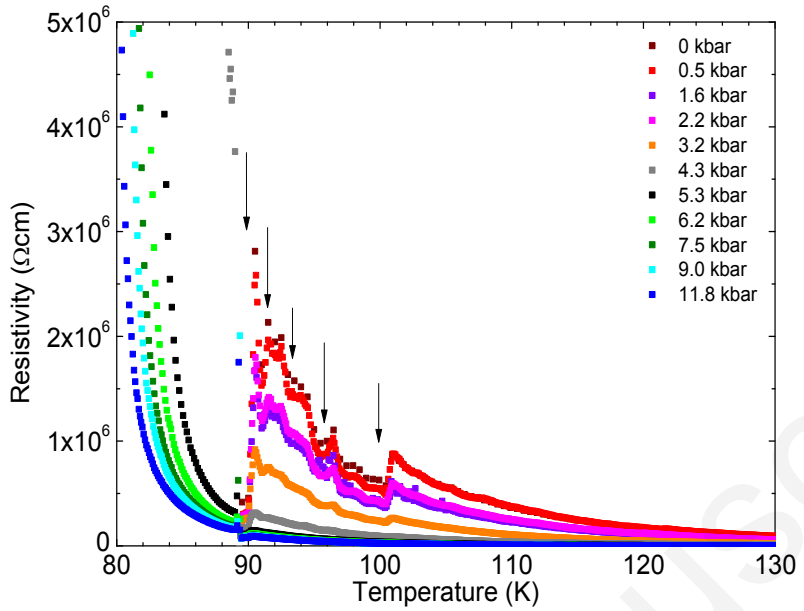
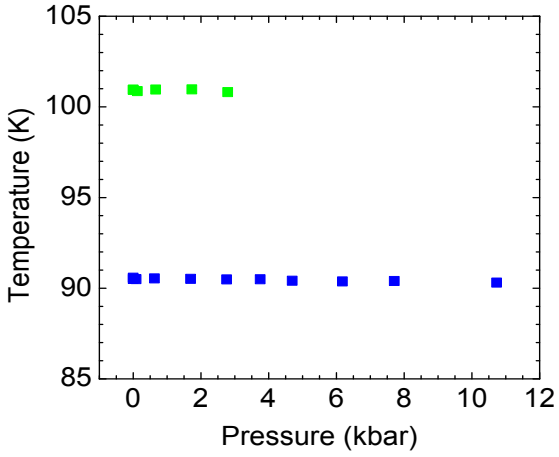


Fig. 2. Temperature dependent electrical resistivity of (EDT-TTF-I_2)$_2$TCNQF measured by the two-probe method in a clamp-type high-pressure cell without the thermal modification of pressure – see text. Jumps of the electrical resistivity are indicated by arrows.

The resistivity jumps – those observed at 100 and 90 K for p=0 (Fig. 1) – are also seen at higher pressures. The pressure dependence of the resistivity measured at the 90 K dip is displayed in Fig. S2 (Supplementary Material). Temperatures of both jumps are nearly pressure independent (Fig. 3), whereas in TTF-CA the jump of resistivity shifts towards higher temperatures when pressure grows[9]. The jump at about 100 K disappears at about 4 kbar but the jump at 90 K is seen up to the highest pressures; the other smaller jumps at 96, 92 and 91 K also disappear above 4 kbar.



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Fig. 3. Temperature of the resistivity jumps as a function of pressure (thermal modifications of pressure are corrected).

The pressure dependence of the electrical resistivity at various temperatures, after correcting the thermal modification of pressure, is shown in Fig. 4. For each temperature, as pressure grows the resistivity considerably decreases by several orders of magnitude and then is nearly pressure independent. Such regime change is qualitatively similar to the 1:1 complexes with N-I transitions, where the turning point was associated with the pressure-induced N-I transition[4,9,8,19]. Assuming a similar interpretation, one can conclude that for lower temperatures the pressure, which is necessary to transform our samples into the ionic phase, is strongly reduced. At about 100 K the N-I transition occurs at p=4.3 kbar and above 200 K the pressure required to transform the crystal into the ionic phase is nearly temperature independent and equals to approximately 7.7 kbar. Since for each temperature the regime change is rather smeared, the pressure, at which the change occurs, was evaluated by crossing two lines, approximating the dependence below and above the turning point (see Fig. 4). After estimating the transition to the ionic phase by this method, a pressure-temperature phase diagram of (EDT-TTF-I_2)$_2$TCNQF can be composed (Fig. 5). We believe that this diagram shows the transition between quasi-neutral and quasi-ionic phases of the complex; the transition is only observed above 4.3 kbar. Qualitatively the diagram is similar to analogous diagrams for the 1:1 salts[9,18], i.e. when pressure grows the transition temperature between both phases also grows. However, it should be stressed that it is not clear whether there is a back bending of the line separating the phases (at about 7.7 kbar), since this bending lies within the limits of experimental errors. It is reasonable to assume that above the pressure 7.7 kbar the crystal is in the quasi-ionic phase in the whole temperature range. Our previous spectroscopic studies under ambient pressure revealed that the degree of charge transfer continuously grows on cooling down to the lowest temperatures, reaching at T = 10 K a value of about 1e[23,24], whereas the present pressure studies show a more or less abrupt transition. This difference can be either related to a specific crystal modifications induced by pressure or the difference between properties of bulk material and microscopic observations by spectroscopic techniques.

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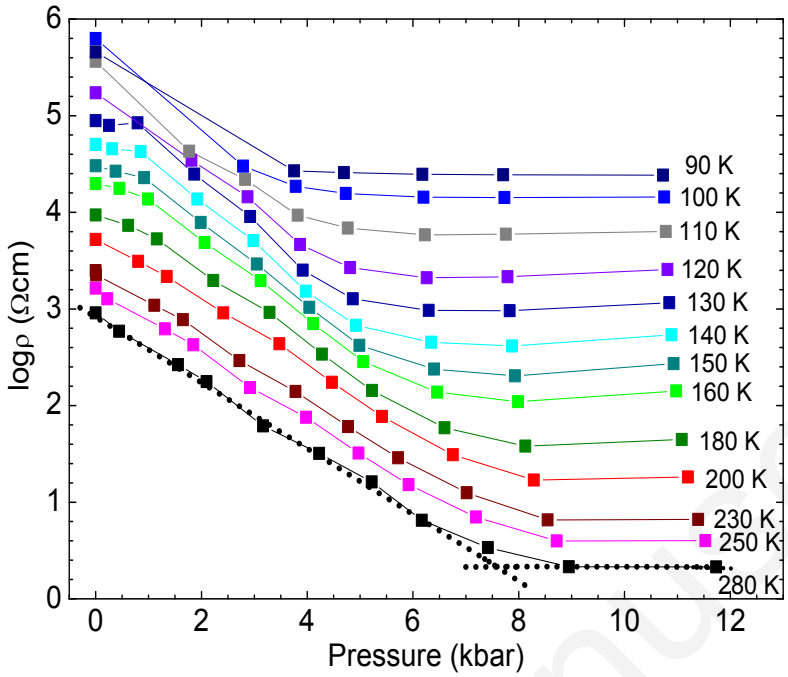
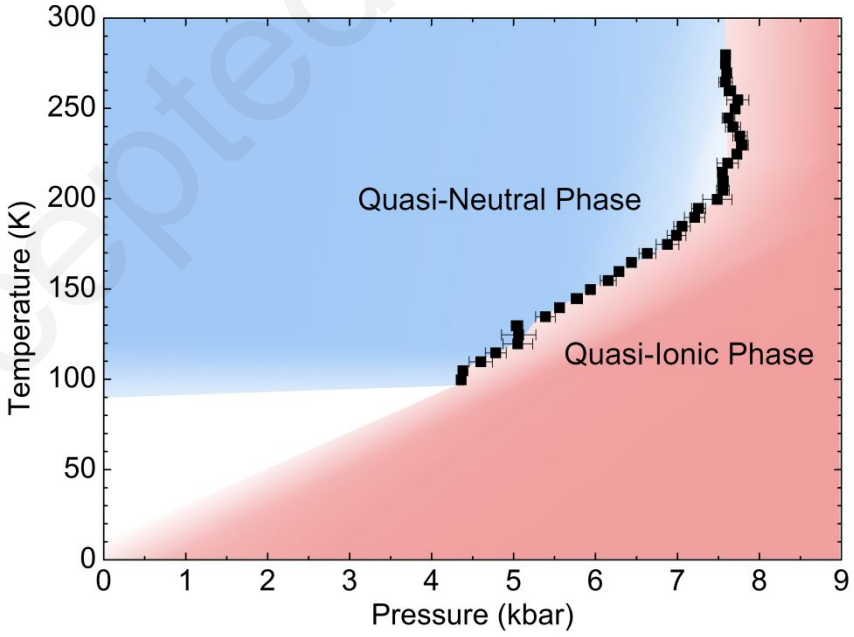


Fig. 4. Resistivity of $(EDT\text{-}TTF\text{-}I_2)_2TCNQF$ as a function of pressure at different temperatures as indicated (thermal change of pressure is corrected). The crossed dotted lines at 280 K illustrate the method used for estimation of the pressure of regime change.



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Fig. 5. Pressure-temperature phase diagram of $(EDT\text{-}TTF\text{-}I_2)_2TCNQF$ as derived from the electrical resistivity data (thermal change of pressure is corrected). The white area corresponds to a gradual neutral-ionic transformation.

Pressure dependence of the activation energies (E_a) as determined from the resistivity curves (Arrhenius plots) is displayed in Fig. 6. Fig. S3 (Supplementary Material) illustrates the method of E_a determination. As mentioned above, there are two activation energies at ambient pressure: 109 meV (E_{a1}) and 86 meV (E_{a2}) above and below 200 K, respectively. Both energies depend on the applied pressure. According to the phase diagram shown in Fig. 5, the crystal is in the quasi-neutral phase up to about 4.3 kbar in the whole studied temperature range. Therefore, we assume that both E_{a1} and E_{a2} are related to the quasi-neutral phase and when pressure grows up to 4.3 kbar these energies increase. For high pressures above about 7.7 kbar the crystal is in the quasi-ionic phase and only one E_a = 125 meV is seen in the whole studied temperature range. In the intermediate pressure range p = 4.3 – 7.7 kbar (see Fig. 5), depending on temperature the crystal is either in quasi-neutral or quasi-ionic phase, therefore two E_a were estimated corresponding to these phases. When pressure increases the E_{a1} of quasi-neutral phase grows and then in the intermediate range above 4.3 kbar decreases, whereas the E_{a2} of quasi-neutral phase increases and then at 4.3 kbar – it is remarkable – smoothly passes into the E_a of quasi-ionic phase. For this reason one can assume that the E_{a2} in quasi-neutral phase below 4.3 kbar is most probably related with the quasi-ionic state. It is important that all the observed activation energies for neutral and ionic states (86-170 meV) are much smaller than the CT excitation energy at ambient pressure (about 500 meV).

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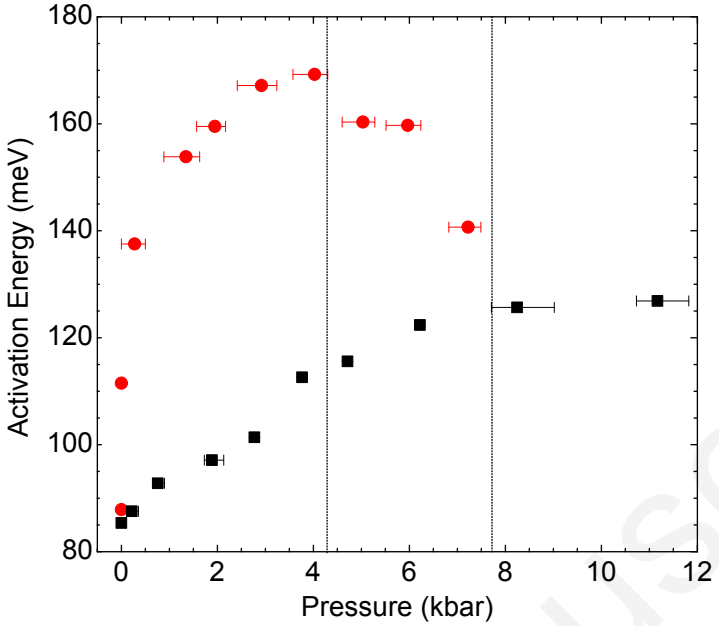


Fig. 6. Pressure dependence of the activation energies of (EDT-TTF-I_2)$_2$TCNQF determined in three regions for: the quasi-neutral phase (0 - 4.3 kbar) two E_a are observed in temperature ranges (300-200 K and 200-100 K); the intermediate phase (4.3-7.7 kbar), i.e. in quasi-neutral phase (upper points) and quasi-ionic phase (bottom points); the ionic phase (above 7.3 kbar) – see text.

Discussion

In 1:1 mixed-stack complexes with N-I transitions, the stacks in the neutral phase are usually uniform and they are distorted in the ionic phase (dimerization). However, in the 2:1 charge-transfer complex (EDT-TTF-I_2)$_2$TCNQF, the stacks are non-uniform already in the quasi-neutral phase at ambient temperature and the molecules are arranged in centrosymmetric units …DAD…. (Fig.7a). Evidently, donor-donor interactions between trimers (Fig. 7c) are different in comparison with intra-trimer donor-acceptor interactions (Fig. 7d). It is remarkable that in (EDT-TTF-I_2)$_2$TCNQF the molecular long axes are parallel, whereas a characteristic feature of other mixed-stack complexes is that the axes are not parallel[29,30]. The mixed-stacks form molecular slabs within the *ab* plane and the neighboring slabs are connected by halogen bonds (Fig. 7b). This interaction is essentially electrostatic in nature and does not include any sizeable overlap interaction which could link the slabs electronically. In a way it can be compared with the weak C-H···O hydrogen bonds observed in TTF-CA between the hydrogen atoms of TTF and

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the oxygen atoms of CA, which become activated upon the N-I transition[31]. For this reason, we assume that the crystal is quasi-one-dimensional.

There is another important difference between 1:1 and 2:1 complexes with mixed-stacks showing the N-I transition. In the 1:1 complexes the transition occurs when the difference between the ionization potential of donor (I_D) and the electron affinity of acceptor (E_A) becomes comparable with the electrostatic Madelung energy (M). Both I_D and E_A are molecular constants, therefore they are independent of temperature but only the energy M is modified due to thermal contraction of the crystal lattice. However, in the case of 2:1 complex one should take into account that the parameter I_D can be also dependent on temperature.

At the N-I transition an electron is transferred from the donor HOMO orbital of EDT-TTF-I_2 to the acceptor LUMO orbital of TCNQF. However, due to interaction between neighboring trimers the HOMO of donors splits into bonding and antibonding orbitals. An electron is transferred from the bonding orbital, whose energy is lower in comparison with the undistorted monomer, therefore the value of I_D increases. When the crystal lattice contracts, the intra-stack transfer integrals grow, both within and between trimers, therefore both M and I_D increase. It is therefore possible that the interplay between M and I_D is a reason why – at ambient pressure in (EDT-TTF-I_2)$_2$TCNQF – the N-I transformation is continuous, as shown by spectroscopic data[23,24]. Such competition between M and I_D should be considered as a specific feature of the 2:1 complexes. On the other hand, there exist a disorder in the (EDT-TTF-I_2)$_2$TCNQF crystal due to the fluorine atom occupancy in TCNQF which is 50 %. This disorder may have also an influence on smearing of the N-I transformation over broad temperature range.

Previous IR studies showed that the charge distribution among EDT-TTF-I_2 molecules is not uniform below $T \approx 100$ K[24]. On the other hand, the X-ray data provided evidence that the TCNQF molecules are located on the inversion center down to T=20 K without any indication of structural phase transition[23]. That is why, on basis of these observations it was suggested that the polarization of donor-acceptor domains in mixed-stacks fluctuates between opposite directions. Within this scenario, taking into account the trimers DAD, one can speculate that the polarization of trimers fluctuates, i.e. the charge density fluctuates between donor molecules. The amplitude of fluctuations increases on cooling down and thus the degree of dynamical trimer distortion grows, as indicated by the intensity increase of IR features related with the electron-molecular

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vibration coupling effect[23,24]. Obviously, the fluctuations in neighboring trimers should be strongly correlated, yielding thus short-living ferroelectric domains with polarization fluctuating between opposite directions.

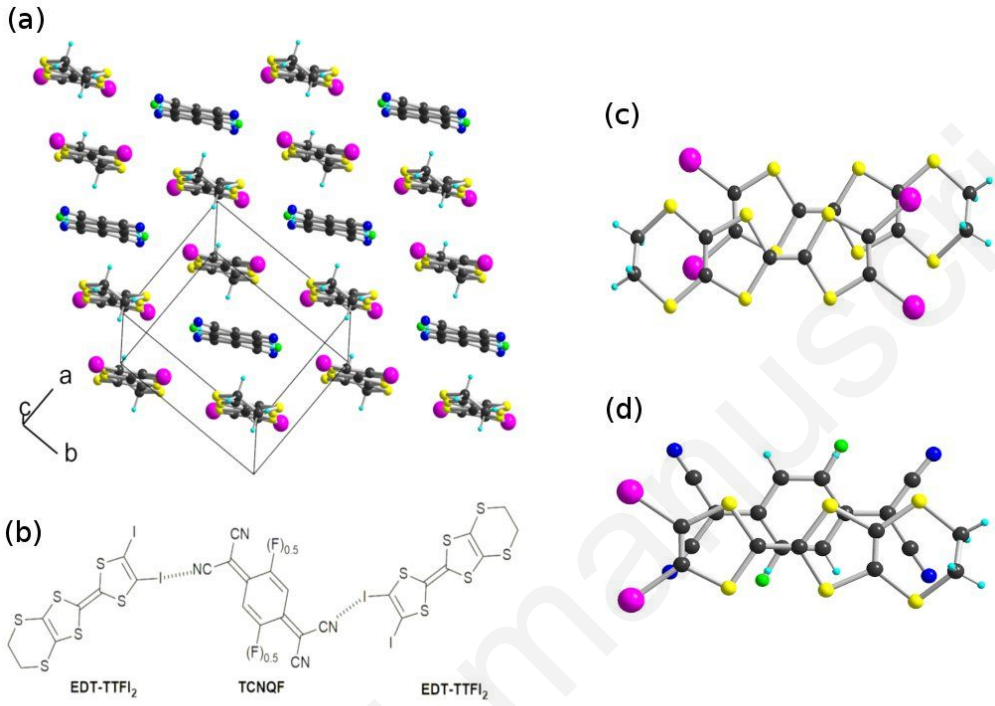


Fig. 7. The $(EDT\text{-}TTF\text{-}I_2)_2TCNQF$ structure of the mixed-stacks with trimeric …DAD… units (a); halogen bonding between the stacks perpendicular to *a*-*b* plane (b); donor-donor overlap between neighboring trimers (c); intra-trimer donor-acceptor overlap (d).

The electrical conductivity of 1:1 mixed-stack complexes in the quasi-neutral phase is determined by the charged N-I domain wall (NIDW) dynamics[20,21]. The neutral and ionic states are almost degenerated, therefore ionic domains can be spontaneously created in neutral stacks. Nevertheless, in the quasi-neutral phase the energy of ionic region per molecule is higher than that one of the neutral region, therefore the ionic domains are of limited size. Such ionic domains of limited size are regarded as NIDW pairs which are responsible for the charge transport. Moreover, it was proposed that the charge transport is primarily determined by thermally activated motions of the existing NIDW pairs but not by the density of existing charge carriers[32]. Similarly, in our compound it is reasonable to assume that both neutral and ionic states coexist in the quasi-neutral phase and the charged NIDW are responsible for the electrical conductivity.

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Within this picture the remarkable decrease of resistivity under pressure can be attributed to an increase of the density of NIDW pairs (Fig. 4), similarly as in 1:1 complexes[4,9,18]. Due to the crystal contraction induced by pressure, the energy difference between neutral and ionic state decreases, therefore the density of ionic domains should grow. When pressure is high enough the saturation of the NIDW density occurs and the crystal is transformed from the mixed-state to a predominantly ionic state, that is observed from the saturation of the resistivity (Fig. 4). The turning point can be related to N-I transition, as in 1:1 complexes. Nevertheless, above the turning point, the resistivity of the 1:1 complexes increases, while in our salt it is more or less constant. On the other hand, in the quasi-ionic state the charge transport is mainly due to spin solitons which are kink-like defects created between domains of opposite polarization. There are two kinds of such solitons with spin "0" (neutral molecule D^0 or A^0) and spin "½" (charged molecule D^+ or A^-) and they both can contribute to the electrical conductivity because in real crystal they bear a fractional charge[32].

As mentioned above, the temperature variations of the electrical conductivity should be attributed to variations of the mobility of existing charged NIDW. Therefore, we can assume that in (EDT-TTF-I_2)$_2$TCNQF the change of E_a at ambient pressure at about 200 K is due to a change of the NIDW mobility. It is possible that the mobility change is due to modification of inter-molecular interactions in the stacks, nevertheless in our compound the influence of inter-columnar halogen bonding should be also taken into account. When pressure increases up to about 4.3 kbar, the density of NIDW grows but their thermally activated motion can be hindered, therefore both E_{a1} and E_{a2} increase in the quasi-neutral phase (Fig. 6). In the quasi-ionic phase above about 7.7 kbar the spin solitons should be responsible for charge transport, as in 1:1 complexes[20,21], therefore the E_a in this phase is to be related to thermally activated motion of these charge carriers (E_a is rather independent on pressure). Within this picture, in the intermediate pressure region (4.3-7.7 kbar), depending on temperature range, the charge transport should be realized either by the charged NIDW or by the spin solitons. As already noticed above, when pressure grows the activation energy E_{a2} of the quasi-neutral phase passes smoothly into the activation energy of the quasi-ionic phase. Such behavior could suggest that the E_{a2} corresponds to soliton transport in the whole pressure range. If it is true one could speculate that even at ambient pressure below about 200 K the charged solitons can also contribute to the electrical conductivity.

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Conclusions

We have shown here that the hydrostatic pressure can induce a N-I transition in the 2:1 mixed-stack complex (EDT-TTF-I_2)$_2$TCNQF. On basis of anomalies in the pressure-dependence of electrical resistivity the pressure-temperature phase diagram was determined. In comparison with TTF-CA – a prototypical material exhibiting the N-I transition – in our complex the transition is not so sharp and takes place rather smoothly. The transition smearing can be related with the fact that in the 2:1 complex not only the Madelung energy M but also the ionization potential of donors I_D can grow as the crystal contracts on temperature decreasing. Furthermore, the charge transport mechanism in (EDT-TTF-I_2)$_2$TCNQF appears to be similar as in 1:1 complexes, i.e. by charged NIDW pairs in the quasi-neutral phase and charged solitons in the quasi-ionic phase. However, our analysis of the resistivity activation energies for various pressures suggests that solitons might also contribute to charge transport below 200 K even at ambient pressure, what is reasonable if we take into account that in our compound the N-I transition undergoes gradually.

Supporting Information

Comparing of electrical resistivity of (EDT-TTF-I_2)$_2$TCNQF measured upon cooling and heating, pressure dependence of resistivity of (EDT-TTF-I_2)$_2$TCNQF at the dip at about 90 K, linear fits of electrical resistivity of (EDT-TTF-I_2)$_2$TCNQF which were made to extract values of activation energies for selected values of hydrostatic pressure.

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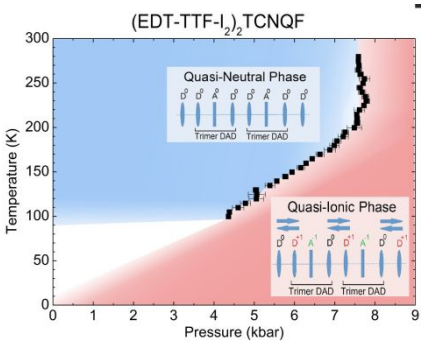
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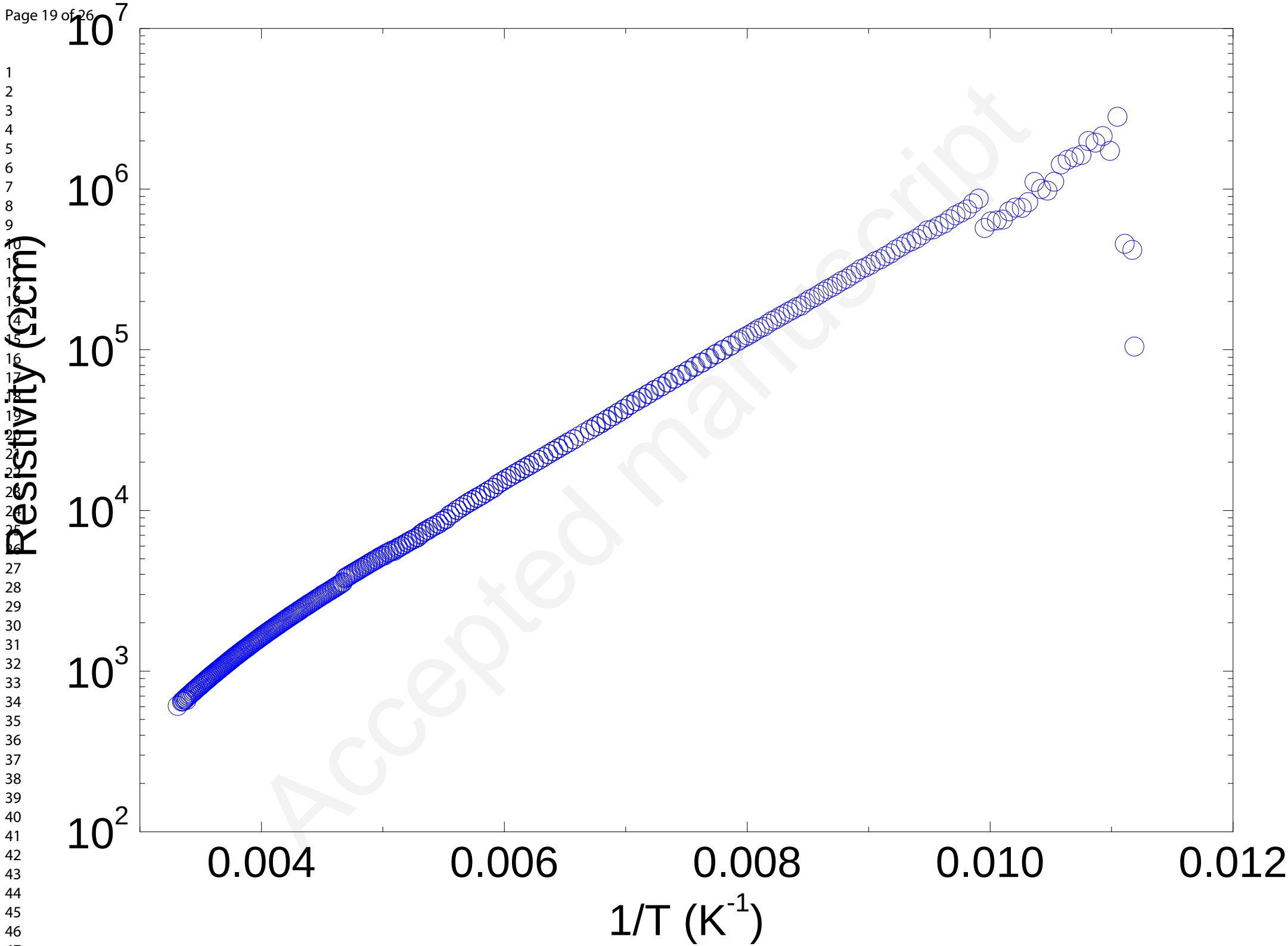
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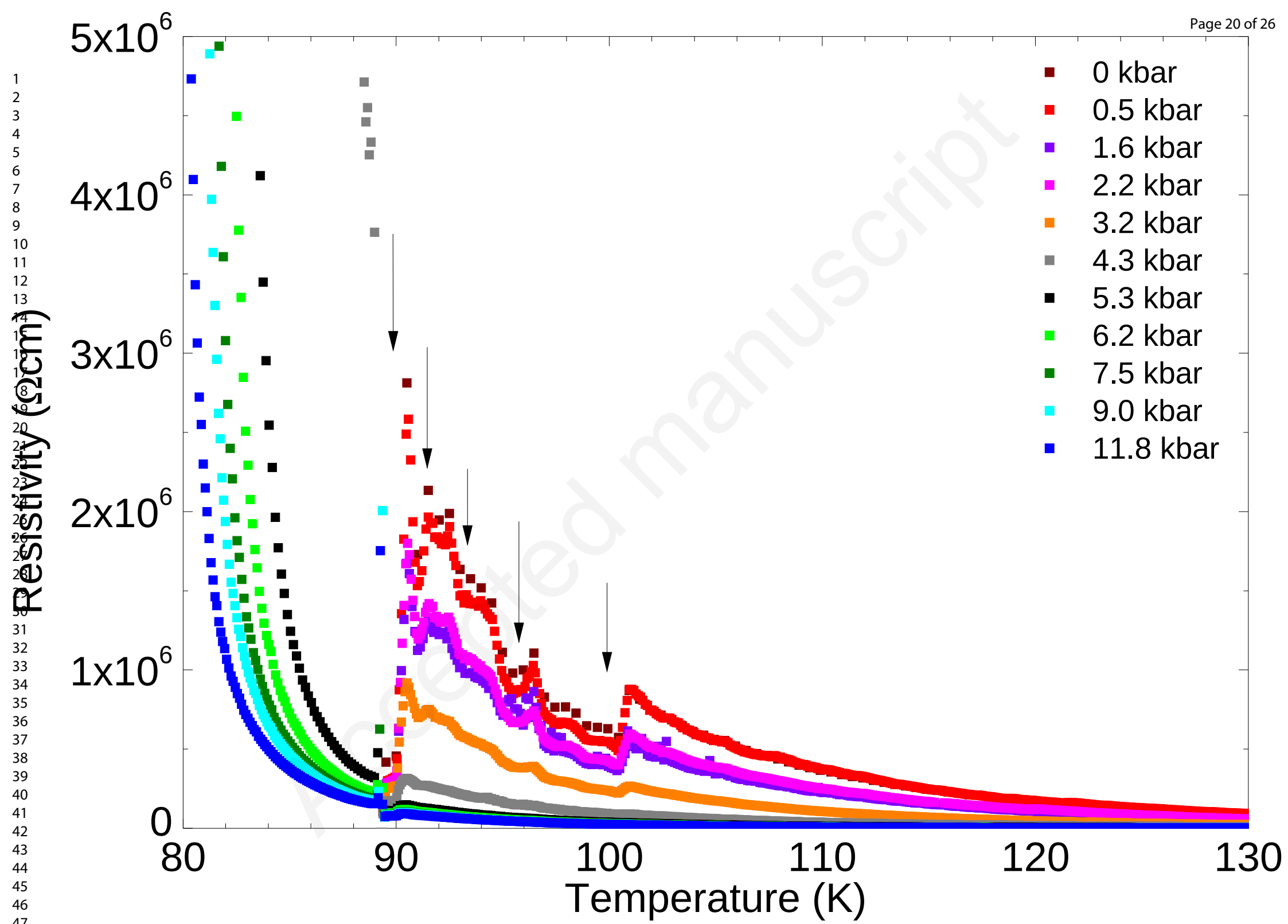
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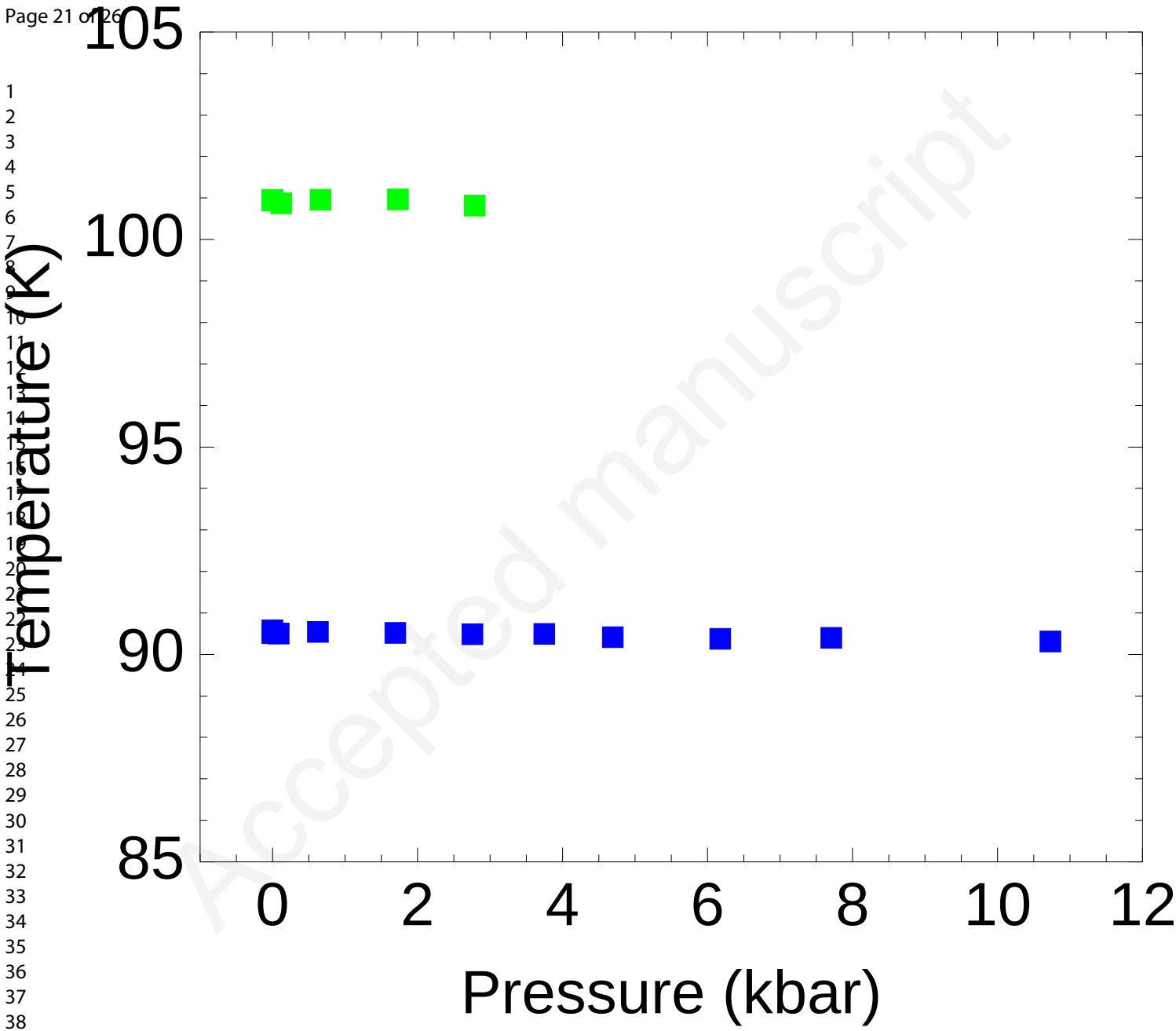
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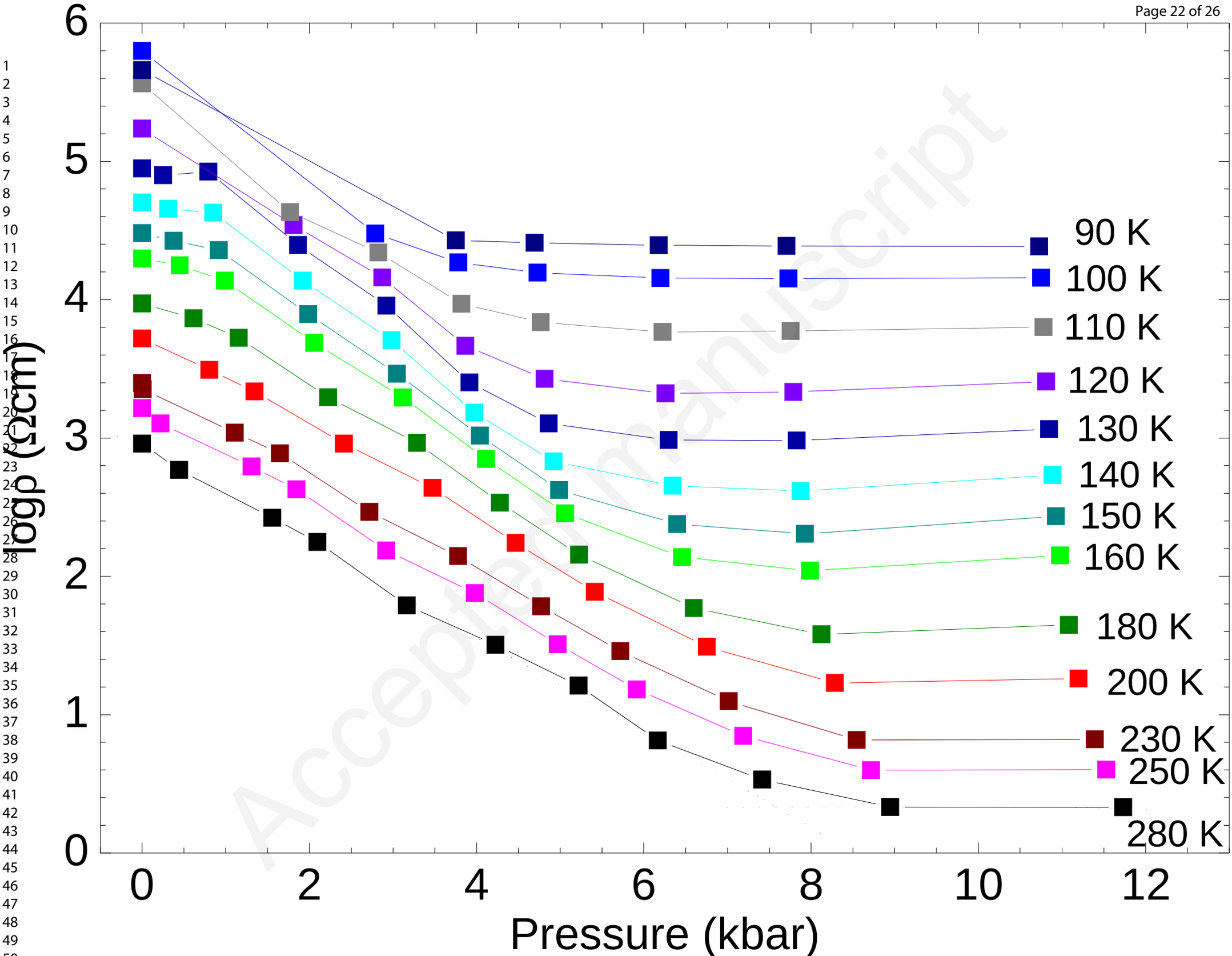
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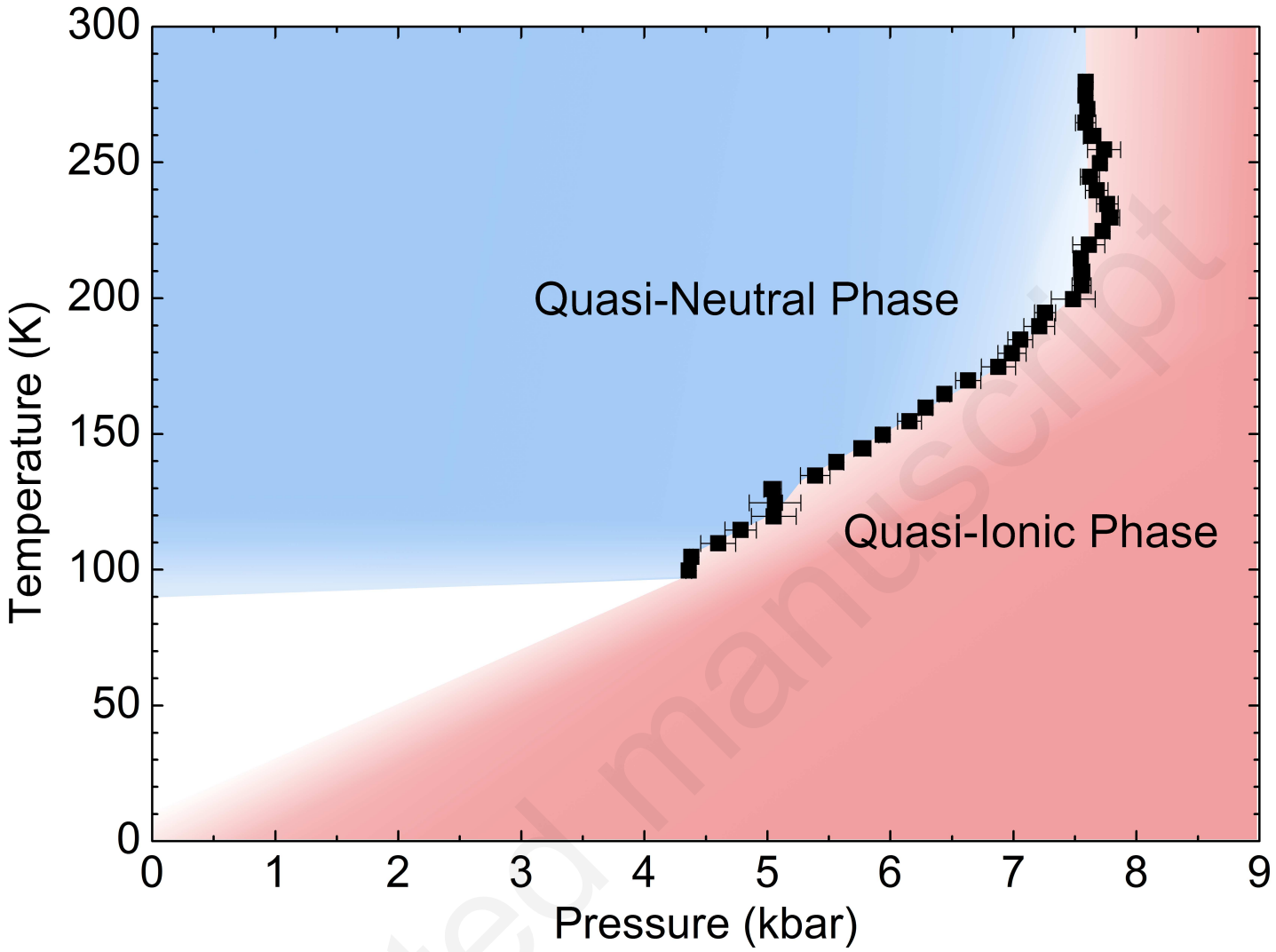
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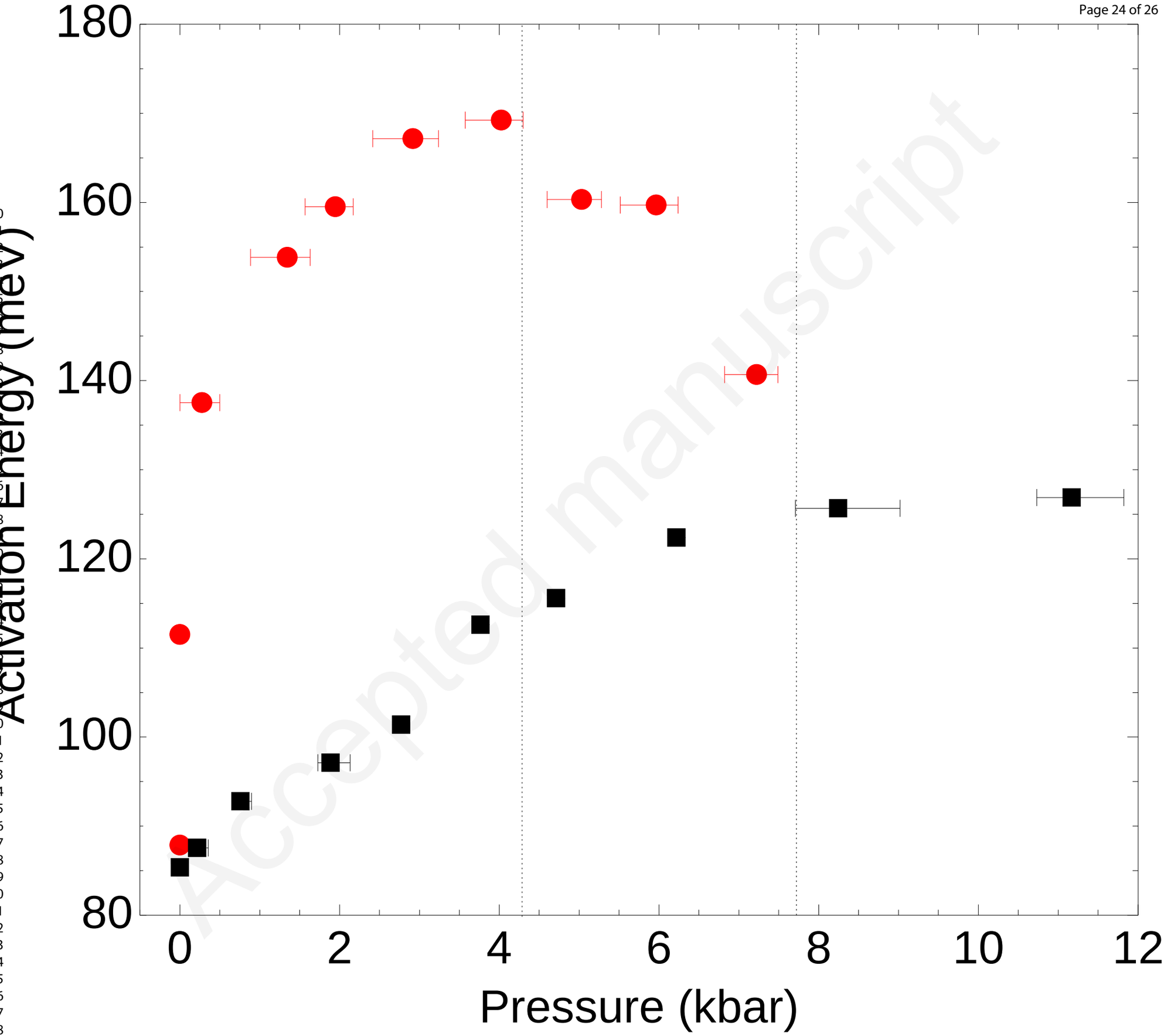
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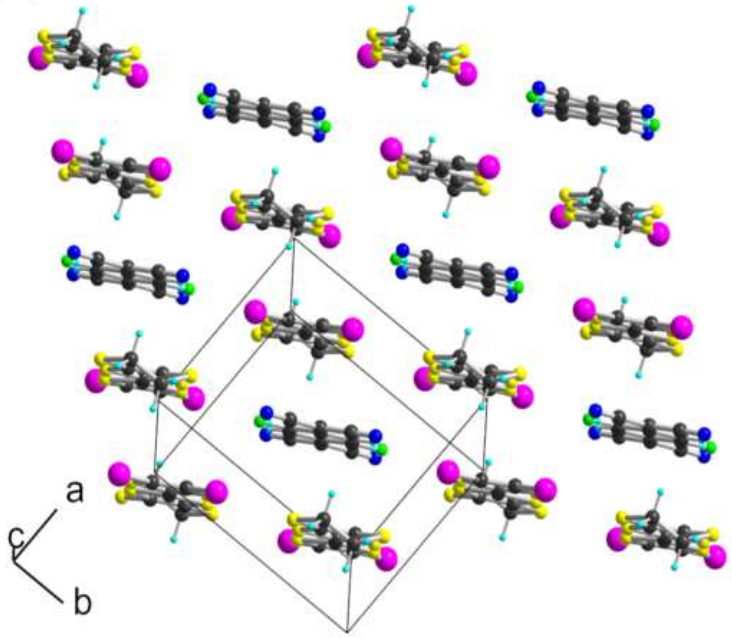


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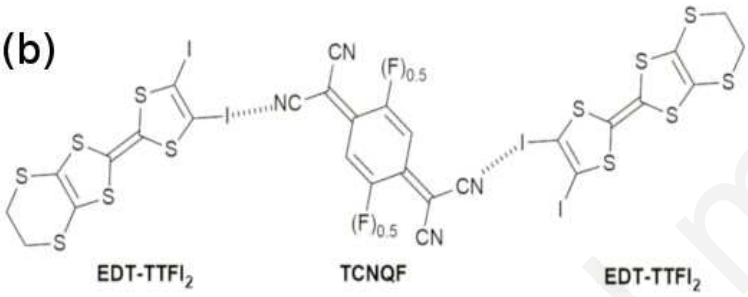


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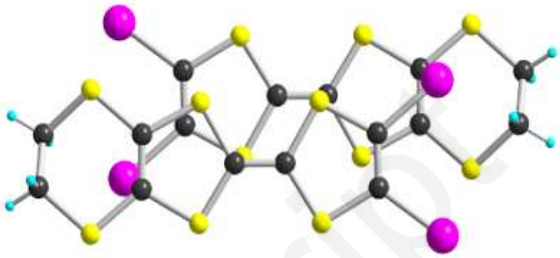
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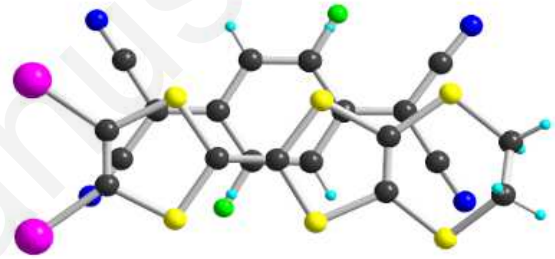
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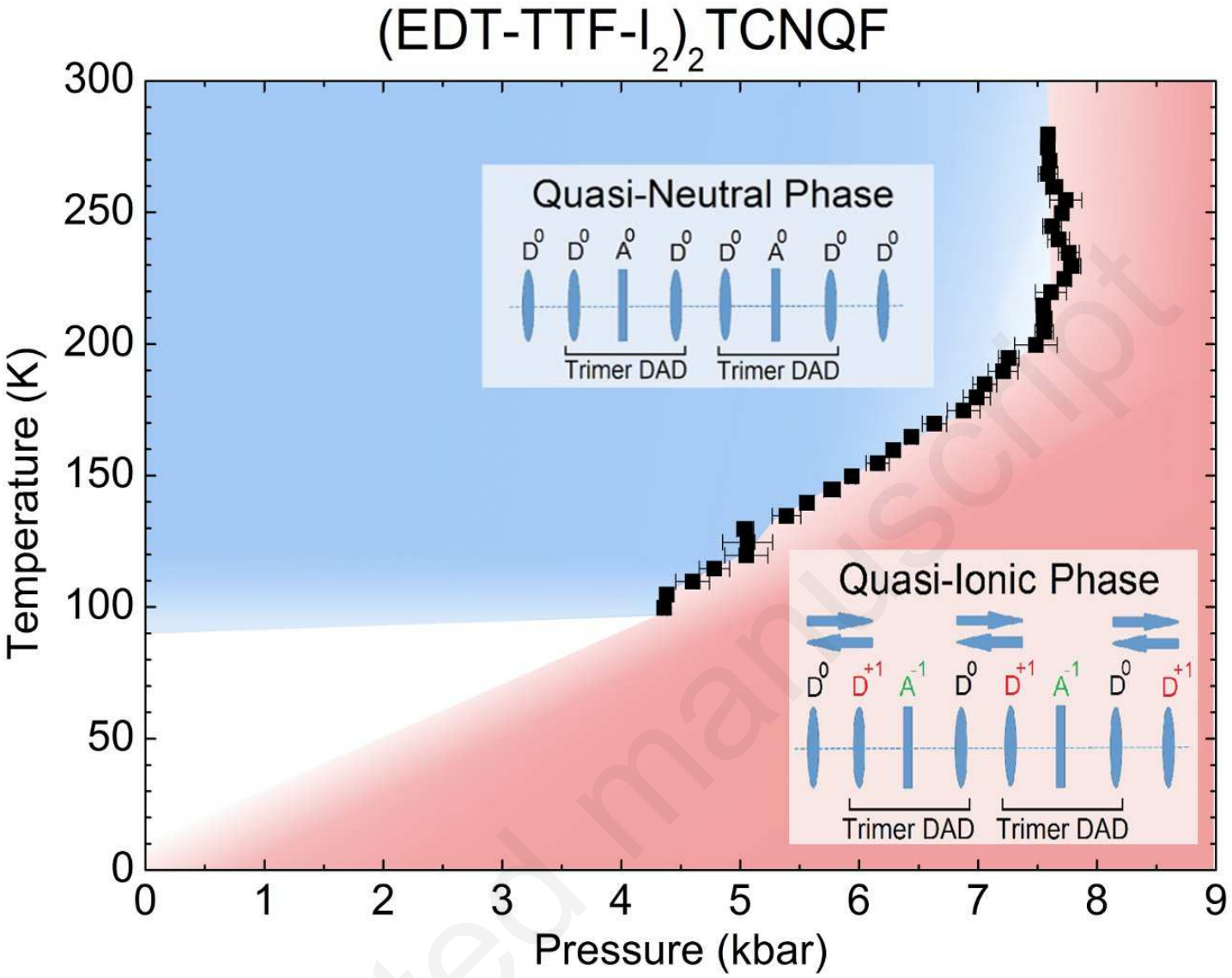
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