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# Electrical and Optical Behavior of One-Dimensional Organic Conductors at High Pressures

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Electrical and optical behavior of 10 one-dimensional organic conductors have been studied at high pressures. The electrical resistivity of the organic conductors decreases with increasing pressure in the low-pressure region and reaches each resistivity minimum. The lowest resistivity of TTF–TCNQ and TTF derivative salts at high pressures is much lower than that of other salts. For conducting TCNQ salts, a pressure-induced absorption band has been observed around $20 \times 10^3$ cm$^{-1}$; it may be assigned to the new charge transfer band between TCNQ. A pressure-induced band is not found in TTF–TCNQ, but the change of spectra with pressure is observed around $12 \times 10^3$ cm$^{-1}$. Above certain pressures the electrical resistivity of the organic conductors increases rapidly with increasing pressure and drifts upward with time. These phenomena arise from the solid phase reaction. The differences of the physicochemical properties of one-dimensional organic conductors will be discussed.

Recently, many one-dimensional organic conductors have been found. The majority of these conducting materials are salts formed from various aromatic cations containing nitrogen or chalcogens and the anion of TCNQ (*1–3*). Complex TCNQ salts in which the ratio of cation to TCNQ is 1 : 2 generally are several orders of magnitude more conducting than simple TCNQ salts of the same cation. NMP– and TTF–TCNQ are simple TCNQ salts, but their conductivities are significantly larger than those of complex salts. Torrance *et al.* (*4*) suggested that the large conductivity of these 1 : 1 salts is attributed to incomplete charge transfer from the aromatic cation to TCNQ.

The degree of the charge transfer in several incomplete TCNQ salts has been estimated from the analysis of an X-ray diffuse scattering (*5–7*). It is suggested that the anionic column consists of a mixed valence stack of TCNQ$^-$ anion and neutral TCNQ molecule, and that the cationic column is constructed from a mixed valence stack of cation and neutral molecule.

The organic donors, TTF, TTT, and their derivatives, react with halogen, forming nonstoichiometric compounds such as TTF–$X_n$ ($X$ = halogen). The mixed valence cation of radical salts cause considerable interest because their conductivities are quite near to those of conducting TCNQ salts (*8, 9*).

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Electrical (*10, 11*), optical (*12, 13*), and magnetic (*14*) properties in one-dimensional organic conductors have been studied at high pressures. Their electrical conductivities increase with increasing pressure in the low-pressure region. Pressure-induced absorption bands in TCNQ salts have been observed at room temperature. The pressure dependence of the absorption edge in TTF–TCNQ has been studied. The metal–insulator transition temperature near 54 K for TTF–TCNQ increases with increasing pressure (*15*).

In this paper, we present some findings on the effect of pressure on the electrical and optical properties in one-dimensional organic conductors and will discuss the differences of their properties.

## Experimental

The molecular structures of the donors and the acceptors used in the experiments are illustrated in Fig. 1. These donors react with the acceptors such as TCNQ and halogen, forming many organic conductors. We have prepared 10 organic conductors according to the literature (*1–3, 16–19*).

Conductivity measurements at high pressure were undertaken using a split sphere apparatus (*20, 21*). The electrical resistivity of the polycrystalline pellets of these compounds was measured as a function of pressure at room temperature. The measurements of absorption spectra up to a pressure of 7 kbar (*22*) were carried out using an optical vessel made of hardened steel.

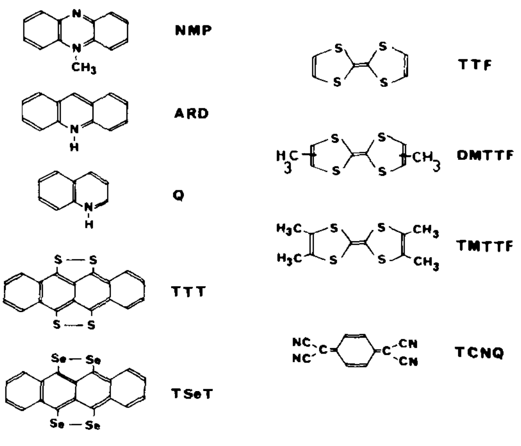

FIG. 1. The molecular structures of the donors and the acceptors used in the experiments.

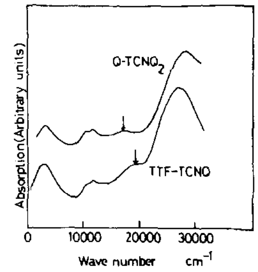

FIG. 2. The absorption spectra of Q–TCNQ$_2$ and TTF–TCNQ.

## Results and Discussion

The absorption spectra in conducting TCNQ salts show striking similarity although their electrical conductivities differ. Figure 2 exhibits the absorption spectra of Q–TCNQ$_2$ and TTF–TCNQ. The character of the optical transitions is discussed by many authors (*23–25*). The absorption band at $26 \times 10^3$ cm$^{-1}$ is identified as the LE band in TCNQ molecules. The band at $5 \times 10^3$

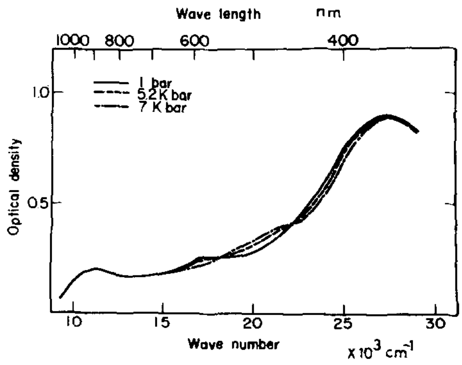

FIG. 3. The effect of pressure on the absorption band of Q–TCNQ$_2$.

$cm^{-1}$ is assigned as the CT band from $TCNQ^-$ anion to neutral TCNQ molecule. It should be noted that the peak of the band indicated by the arrow in the spectrum of Q–$TCNQ_2$ is located slightly apart from that of TTF–TCNQ at atmospheric pressure. Figure 3 shows the effect of pressure on the absorption band of Q–$TCNQ_2$. The absorption intensity of the peak around 17 × $10^3$ $cm^{-1}$ decreases with increasing pressure, and a new pressure-induced band appears around 20 × $10^3$ $cm^{-1}$. The change in the absorption spectra with pressure is reversible. On the other hand, the band indicated by the arrow in TTF–TCNQ is insensitive to pressure. The band of Q–$TCNQ_2$ indicated by the arrow is clearly distinct from that of TTF–TCNQ at high pressures. Therefore, the character of the bands in both salts must be essentially different from each other.

A similar pressure-induced absorption band has been observed in many other conducting TCNQ salts such as NMP–TCNQ (*12*). Oohashi and Sakata have suggested that the pressure-induced band around 20 × $10^3$ $cm^{-1}$ may be assigned to 8–9′ CT transition from TCNQ anion to neutral molecule (*25*). The absorption band indicated by the arrow in TTF–TCNQ may correspond to the pressure-induced band in many TCNQ salts. Since the TCNQ–TCNQ interplanar spacings within the stack is very short for TTF–TCNQ, the CT band seems to be observable even at atmospheric pressure. It can be seen from Table I that generally, the smaller the intermolecular spacings within the stacks, the larger the electrical conductivities of the TCNQ salts. The resistivity of conductive TCNQ salts in which the pressure-induced absorption band has been observed rapidly decreases in the low-pressure region. In such salts, charge–transfer interactions between TCNQ molecules could become much stronger by compression. Therefore, we suggest that the new charge transfer bands around 20 × $10^3$ $cm^{-1}$ in conducting TCNQ salts are closely related to their electrical conductivities.

Figure 4 shows the effect of pressure on the absorption spectra of TTF–TCNQ. The absorption band around 12 × $10^3$ $cm^{-1}$ (840 nm) changes with increasing pressure. In a previous paper we have reported the absorption spectra of NMP–TCNQ at high pressure (*26*). The absorption spectra is similar to that of Q–$TCNQ_2$. The absorption band around 12 × $10^3$ $cm^{-1}$ in these salts is insensitive to pressure. The electronic state of NMP–TCNQ is markedly different from that of TTF–TCNQ at high pressure.

The physical properties of organic con-

TABLE I

PHYSICAL PROPERTIES OF CONDUCTING TCNQ SALTS

| | Interplanar spacing (Å) | | Conductivity along the conductive axis ($\Omega^{-1}$ $cm^{-1}$) | Density ($g/cm^3$) | Degree of charge transfer ($\rho$) |
|---|---|---|---|---|---|
| | TCNQ | Donor | | | |
| NMP–TCNQ | 3.26 | 3.36 (*34*)[a] | $1 \sim 3 \times 10^2$ (*16, 26*) | 1.43 (*34*) | $0.6 \sim 0.9$ (*6, 7*) |
| TTF–TCNQ | 3.17 | 3.48 (*43*) | $5 \sim 10 \times 10^2$ (*2*) | 1.62 (*43*) | $0.55 \sim 0.59$ (*4*) |
| HMTSeF–TCNQ | 3.21 | 3.61 (*33*) | $\sim 2 \times 10^3$ (*32*) | 2.09 (*33*) | 0.74 (*45*) |
| Q–$TCNQ_2$ | 3.22 | 3.50 (*35*) | $10^2$ (*1*) | 1.398 (*35*) | |
| ARD–$TCNQ_2$ | 3.25 | 3.42 (*36*) | $10^2$ (*44*) | 1.389 (*36*) | |
| TTT–$TCNQ_2$ | 3.18 | 3.52 (*40*) | $10^2$ (*40*) | 1.41 (*40*) | |

[a] Reference number in parentheses.

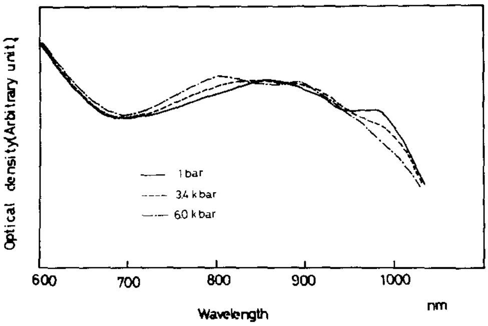

FIG. 4. The effect of pressure on the absorption band of TTF–TCNQ.

ductors are summarized in Table I. The conductivities along the conductive axis cf the single crystals are 100 ~ 400 $\Omega^{-1}$ cm$^{-1}$ for NMP-TCNQ and 500 ~ 1000 $\Omega^{-1}$ cm$^{-1}$ for TTF–TCNQ at atmospheric pressure. The interplanar spacing between the TCNQ molecules in TTF–TCNQ, 3.17 Å, is much shorter than that in NMP–TCNQ, 3.26 Å. Figure 5 exhibits the electrical resistivity of NMP- and TTF–TCNQ at high pressures. The electrical resistivity decreases with increasing pressure in the low-pressure region and reaches each resistivity minimum. At higher pressures the resistivity increases with increasing pressure. The lowest resistivity of NMP–TCNQ is about 10 times that of TTF–TCNQ at high pressure. These values are given in Table I.

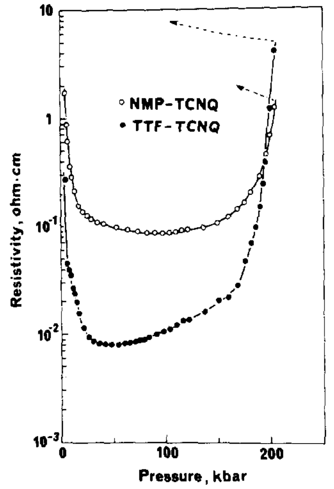

FIG. 5. The electrical resistivity of NMP– and TTF–TCNQ at high pressure.

Tanaka *et al.* have found that the values of calculated transfer integral (*t*) for TCNQ are 0.1089 eV in NMP–TCNQ, and 0.1377 eV in TTF–TCNQ (*24*). Assuming that the bandwidth is 4*t*, we obtain bandwidths of about 0.44 and 0.55 eV for TCNQ in NMP-TCNQ and TTF–TCNQ, respectively. Similar results have been obtained by many authors (*27, 28*). Herman *et al.* estimated the bandwidth of TTF to be 0.48 eV (*28*). On the other hand, since the interplanar distance between NMP cations (3.36 Å) is very long, the cation bandwidth must be narrow. On the basis of previous studies of band structures in aromatic hydrocarbon crystals (*29*), we can estimate the bandwidth of about 0.1 eV for NMP cation. The bandwidths in the b direction for TTF and TCNQ increase considerably with increasing presssure (*13*). The bandwidths of TTF–TCNQ could increase faster with decreasing lattice parameter than those of NMP–TCNQ.

Intercolumnar interactions in conducting TCNQ salts are closely related to a magnitude of the electrical conductivity. HMT SeF–TCNQ remains metallic character even at very low temperature (*30*). The nearest Se—N distance between HMTSeF and TCNQ is 3.10 Å. Se—N contacts in HMTSeF–TCNQ are much shorter compared with S—N contacts in TTF–TCNQ (*31*). Interatomic distances between atoms of adjacent column in NMP–TCNQ are not given in the literature (*32*). The close approach distances in Q– and ARD–TCNQ$_2$ occur between the nitrogen atom of cyano group of TCNQ and the nitrogen atom of the cations (*33, 34*). These distances are longer than the sum of van der Waals radii. But there is a methyl group on each phenazinium cation, so the intercolumnar interactions in NMP–TCNQ must be weaker than those in Q– and ARD–TCNQ$_2$.

The metal–insulator transition temperature near 54 K for TTF–TCNQ increases with increasing pressure (*15*). This suggests that the interchain coupling between TTF and TCNQ columns is important in the salt. The intermolecular S—N distance in TTF–TCNQ is shorter than the sum of the van der Waals radii. Since the lattice constant along the *a* axis at 10 kbar is estimated to be about 98% of that at atmospheric pressure (*13*), intercolumnar interaction in TTF–TCNQ increase considerably with increasing pressure. The differences in the conductivity of NMP–TCNQ and TTF–TCNQ at high pressure are due mainly to those of the bandwidths and the intercolumnar interactions.

Above the minimum pressure shown in Table II, the electrical resistivity of the specimen increases rapidly with increase in the pressure and drifts upward with time. As is shown by the broken curves in Figs. 5, the electrical behavior is irreversible. These phenomena arise from the solid phase reaction. Pressure-induced solid phase reactions for TCNQ salts have already been investigated by Drickamer *et al.* (*35*) and us (*36*). The electronic absorption peaks at 300 ~ 900 nm and the infrared spectra on the basis of the C≡N stretching vibration both disappear under very high pressures. The fact seems to indicate an occurrence of reaction between C≡N bonds in adjacent TCNQ molecules. The interplanar distances between TCNQ molecules in conductive TCNQ salts seem to be closely correlated with the pressure-induced solid phase reaction.

Figure 6 shows the pressure dependence on the electrical resistance along the *b* axis of single crystal of TTF–TCNQ at liquid nitrogen temperature. The resistance measurements at high pressure and at low temperature were carried out using Brigman type apparatus developed for low temperature experiments (*37*). Above about 25 kbar the resistance increases with increasng pressure. The electrical behavior is irreversible for rising and releasing pressure. The electrical resistances of many conducting TCNQ salts at 77 K do not increase with pressure even at very high pressure (*10, 35*). The behavior of the pressure-resistance relation in TTF–TCNQ at 77 K is different from that of other conducting TCNQ salts. The pressure-induced solid phase reaction is observed in TTF–TCNQ even at 77 K.

Figure 7 exhibits the effect of pressure on the resistivity of TMTTF– and DMTTF–

TABLE II

LOWEST RESISTIVITY OF ORGANIC CONDUCTORS AT HIGH PRESSURES

| Salts | Lowest resistivity Ω · cm | Pressure (kbar) |
|---|---|---|
| NMP–TCNQ | $9 \times 10^{-2}$ | 94.0 ± 3.5 |
| TTF–TCNQ | $8 \times 10^{-3}$ | 43.0 ± 3.0 |
| DMTTF–TCNQ | $7 \times 10^{-3}$ | 43.0 ± 3.0 |
| TMTTF–TCNQ | $7 \times 10^{-3}$ | 43.0 ± 3.0 |
| ARD–TCNQ$_2$ | $3 \times 10^{-2}$ | 69.5 ± 3.5 |
| Q–TCNQ$_2$ | $1 \times 10^{-1}$ | 41.0 ± 3.0 |
| TTT–TCNQ$_2$ | $4 \times 10^{-2}$ | 90.5 ± 3.5 |
| TSeT–TCNQ$_2$ | $4 \times 10^{-2}$ | 54.0 ± 3.5 |
| TTF–Br$_{0.8}$ | $1 \times 10^{-1}$ | 18.0 ± 1.0 |
| TTF$_7$–I$_5$ | $4 \times 10^{-2}$ | 41.0 ± 3.0 |

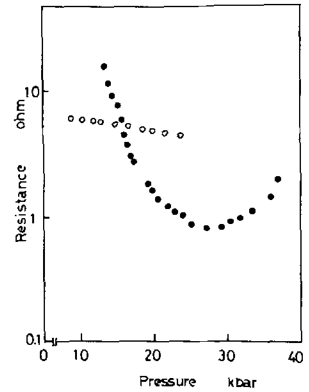

FIG. 6. The pressure dependence of the electrical resistance along the *b* axis of single crystals of TTF–TCNQ at 77 K.

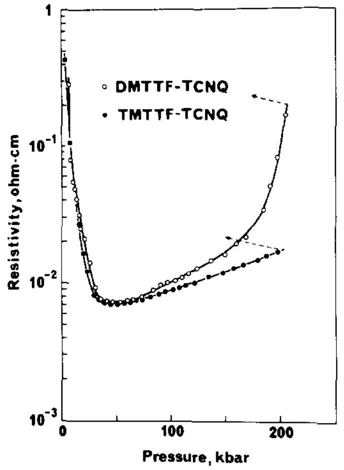

FIG. 7. The electrical resistivity of TMTTF- and DMTTF-TCNQ at high pressure.

TCNQ. The behavior of the pressure-resistivity relation in these salts is almost identical with that of TTF–TCNQ.

The pressure dependence of the resistivity of Q- and ARD–$TCNQ_2$ is shown in Fig. 8. The lowest resistivity of Q–$TCNQ_2$ at high pressure is larger than that of ARD–$TCNQ_2$.

The electrical conductivity of single crystals of TTT–$TCNQ_2$ is about $10^2\ \Omega^{-1}\ cm^{-1}$ along the conductive axis. The interplanar spacing TCNQ–TCNQ and TTT–TTT in the stacks have the values 3.18 and 3.52 Å, respectively (*38*). Figure 9 shows the resistivity of TTT- and TSeT–$TCNQ_2$ at high pressures. The lowest resistivities of these salts at high pressure is much larger than that of TTF–TCNQ. The charge is almost completely transferred from cation to TCNQ in these complex salts because the ionic potentials of TTT and TSeT molecules are small (*39*). The result of resonance Raman spectra in TTT–$TCNQ_2$ suggests that there are few neutral molecules within cation stacks (*40*). Thus, the cationic column hardly contributes to the electrical conductivities of these complex salts although $TTT^+$ and $TSeT^+$ cations have an open-shell electronic structure.

As is shown in Table I, the electrical conductivity of complex TCNQ salts are about $10^2\ \Omega^{-1}\ cm^{-1}$ at atmospheric pressure. The complex salts, generally, show larger conductivity than the corresponding simple salts. The TCNQ stacks in complex salts consist of neutral TCNQ and anionic TCNQ molecule. The Coulomb repulsion within TCNQ stacks is considerably small compared with that in the simple salts.

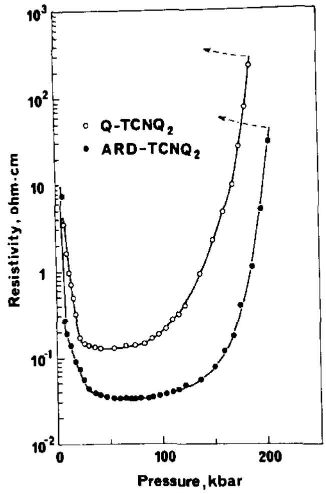

FIG. 8. The electrical resistivity of Q- and ARD–$TCNQ_2$ at high pressure.

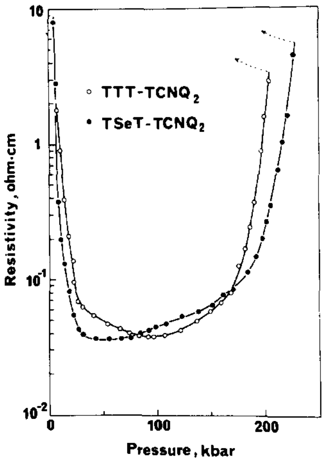

FIG. 9. The electrical resistivity of TTT- and TSeT–$TCNQ_2$ at high pressure.

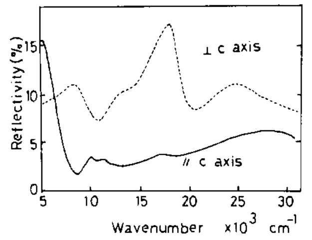

FIG. 10. Reflection spectra of TTT–TCNQ$_2$ single crystals: --- perpendicular to the stacking axis ($c$ axis); —parallel to the stacking axis ($c$ axis).

However, as seen from Tables I and II, the incomplete simple salts such as TTF–TCNQ are more conductive than complex salts even at high pressures. This difference in the conductivity arises mainly from the fact that the conducting electron in the simple salts can move within both TCNQ and cationic stacks; on the contrary, the electron in complex salts is difficult to move within cationic columns. Further, although TTT–TCNQ$_2$ has heavy atom as sulfur, its density is smaller than that of NMP–TCNQ. The molecular packing in the crystal must be loose. This is also predictable from the crystal structure of TTT–TCNQ$_2$ (*38*). The interchain coupling between TCNQ and cation chains in complex salts is weaker than that in incomplete simple salts. Considering these points, we can understand that complex salts are less conductive than incomplete simple salts even at high pressure.

Figure 10 shows the polarized reflection spectra of single crystals of TTT–TCNQ$_2$. These spectra are similar to the solid state spectra of TTT$_2$I$_3$ that have been observed by Kamarás and Grüner (*41*). But the reflection peaks around 10 ~ 12 and 5 × 10$^3$ cm$^{-1}$ parallel to the stacking axis have also been observed in many conducting TCNQ salts. Since it is expected that there are few neutral molecules within TTT cation stacks, the reflection band near 5 × 10$^3$ cm$^{-1}$ may be assigned to CT transition from the TCNQ$^-$ to TCNQ molecule. Figure 11 shows the effect of pressure on the absorption spectra of TTT–TCNQ$_2$. The 10 ~ 12 × 10$^3$ cm$^{-1}$ band does not depend on pressure. As mentioned above, the 10 ~ 12 × 10$^3$ cm$^{-1}$ band in many TCNQ salts is not sensitive to pressure. Thus, this band in TTT–TCNQ$_2$ is identified to the band from TCNQ. The reflection peaks perpendicular to the stacking axis were found at 25, 18, 13.5, and 8 × 10$^3$ cm$^{-1}$. The 25, 13.5, and 8 × 10$^3$ cm$^{-1}$ bands have not been observed in TCNQ salts. The 18 × 10$^3$ cm$^{-1}$ band shifts toward low energy. Similar behavior was not observed in many TCNQ salts. Considering these points four reflection peaks may be ascribed to the transition from the TTT$^+$ cation.

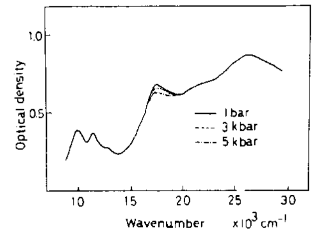

FIG. 11. Absorption spectra of TTT–TCNQ$_2$ at high pressure.

The mixed valence characters in the TTF–halide system have been discussed by several authors (*42*). TTF stacks in cation radical salts such as TTF–Br$_{0.76}$ may be viewed as containing both neutral TTF and cationic TTF$^+$ molecules on a short time scale. The magnitudes of the room temperature conductivities in cation radical salts are high and range from 200 ~ 500 $\Omega^{-1}$ cm$^{-1}$ (*8*, *9*). Figure 12 exhibits the resistivity of TTF–Br$_{0.8}$ and TTF$_7$–I$_5$ at high pressure. The electrical resistivity decreases with increasing pressure in the low-pressure region and reaches the resistivity minimum. At higher pressures the resistivity increases with increasing pressure. It should be noted that the lowest resistivity of the cation radical salts is comparable to that of complex TCNQ salts at high pressure. The electrical conductivity of TTF salts is

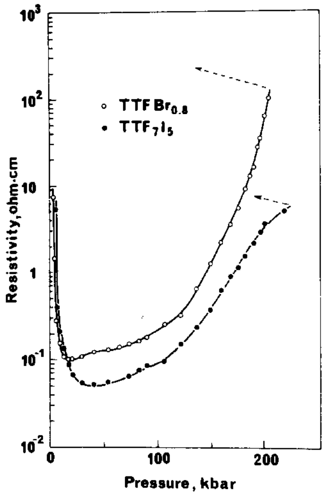

FIG. 12. The electrical resistivity of TTF–Br$_{0.8}$ and TTF$_7$–I$_5$ at high pressure.

significantly smaller than that of TTF–TCNQ. This may arise from the fact that the conducting electron in TTF halides can move only within the cationic column.

Above $P_{\min}$, the resistance of TTF salts increases rapidly with increasing pressure and drifts upward with time at room temperature. As is shown by the broken curves in Fig. 10, irreversible behavior is observed also for these salts. These phenomena may be due to solid phase reaction of a new type, although its mechanism is not fully elucidated at present.

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