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HIGH-PRESSURE CONDUCTIVITY AND STRUCTURE OF HMTSF-TCNQ[‡]

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Abstract Four-probe resistivity measurements on organic conductors have been extended to 6 GPa. The organic metal HMTSF-TCNQ appears to undergo a phase transition to a three-dimensionally ordered conducting state near 4 GPa. X-ray and Raman scattering confirm the transition. Unexpectedly, the degree of charge transfer in HMTSF-TCNQ is relatively insensitive to pressure.

Both the high compressibility of the low-dimensional organic conductors and the dependence of their properties upon a delicate balance of large energies[1] makes one expect that the application of high pressure could significantly alter their behavior. Indeed, it has been found that relatively moderate pressures ($P < 1.5$ GPa) can induce significant changes including the production of superconductivity [2] and changes in the degree of band filling (charge transfer) [3]. Here we study the high-pressure electrical resistivity, Raman scattering and X-ray scattering of one such material HMTSF-TCNQ. One motivation was a desire to monitor the behavior of a material as the degree of charge transfer is forced towards unity through high pressure. Surprisingly, we find that in the pressure range 0-10 GPa there is no evidence for a substantial charge transfer increase. This is contrary to expectations based upon low pressure experiments performed on TTF-TCNQ [3]. We did find however, indications for two high pressure, room-temperature transitions.

Single-crystal electrical conductivity measurements on these types of materials were previously limited to hydrostatic pressures of 3.5 GPa [2]. A new technique has been developed to study the high-pressure electrical transport properties of these fragile crystals which uses the diamond-anvil pressure cell [4]. This technique allows hydrostatic 4-probe resistivity measurements to be made on single-crystal samples in the 0-6 GPa pressure range.

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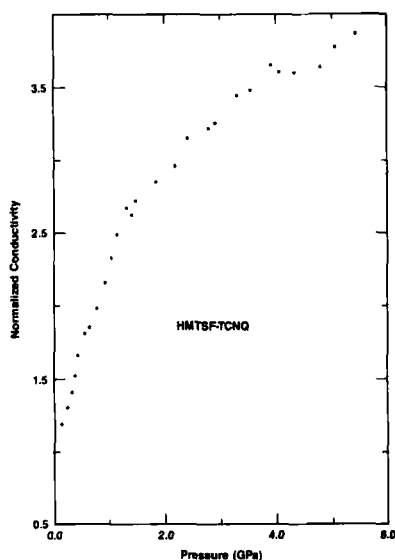


Fig. 1 Normalized conductivity vs. pressure.

Low-pressure data show a positive $d\sigma/dP$ (σ = conductivity) in quantitative agreement with a previous study [2]. As seen in Fig. 1, the data show a change in slope at about 2 GPa closely corresponding to the pressure at which changes in $d\bar{\nu}/dP$ are seen in the Raman scattering.

Higher-pressure data in Fig. 1 suggests structure at $P = 4$ GPa. Repeated experiments on several samples confirm a region of .7 GPa where $d\sigma/dP = 0$. It is at 4 GPa where both Raman and X-ray scattering indicate that a significant transition takes place. Note that at the highest pressures the room temperature conductivity can exceed $7500 \Omega \text{ cm}^{-1}$.

The results from the high-pressure Raman scattering study are shown in Fig. 2. In this study we examined the behavior of four modes, each of which is assigned to a totally symmetric vibrations of the TCNQ molecule. Their frequencies at $P = 0$ are 716.5, 967.5, 1412.5, and 1602.5 cm^{-1} . The experimental techniques have been described elsewhere [5].

There are two important pressures at which abrupt changes take place. At $P = 2$ GPa changes in $d\bar{\nu}/dP$ for two of the modes are found (Fig. 2); however, there are no accompanying changes in linewidth. Then, at $P = 4$ GPa we find that the 716.4 and 1412.5 cm^{-1} modes split into well resolved doublets and although it is difficult to determine definitely, there may be hysteresis in the transition. In the same pressure range the linewidth of the 1602.5 cm^{-1} mode increases whereas that of the 967.5 cm^{-1} one remains narrower than the spectrometer resolution.

The X-ray scattering measurements were made on a single-crystal sample which was mounted in a miniature diamond anvil pressure cell. We made two types of measurements: crystallographic ones, i.e., unit cell symmetry and size, and diffuse scattering ones. In the first instance, we found the compressibility to be highly anisotropic and a smooth function of pressure, but there was no evidence in the sub-structure scattering for a symmetry change in the pressure range studied, $0 < P < 5$ GPa.

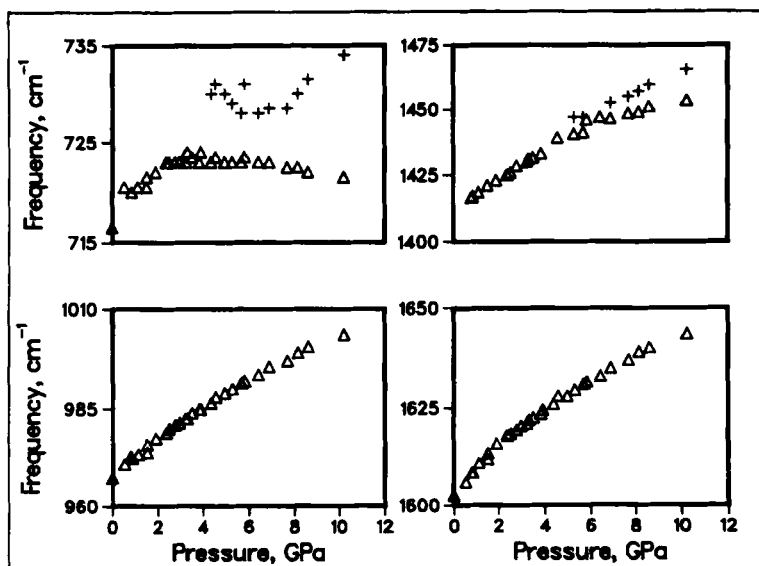


Fig. 2 Dependence of vibrational frequencies on pressure.

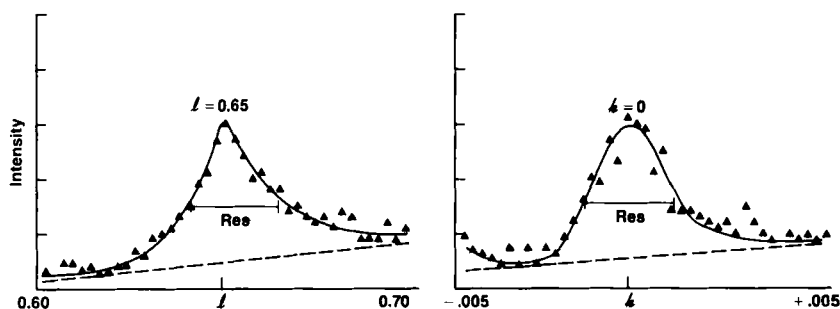


Fig. 3 X-ray scattering from HMTSF-TCNQ at 5 GPa (solid line) and 3 GPa (dashed line).

For the diffuse scattering studies we utilized a rotating-anode Mo X-ray source configured to give a Gaussian resolution function with FWHM of $d0_h = 0.05 \sin\theta \text{ \AA}^{-1}$, $d0_k = 0.1 \text{ \AA}^{-1}$, and $d0_l = 0.05 \cos\theta \text{ \AA}^{-1}$. Geometric constraints limited our measurements to the $h0l$ section, and within that plane, an extensive search was made for super-structure scattering at two pressures, 3 and 5 GPa.

For $P = 5$ GPa we found a new, incommensurate peak at $l = 0.65$ whose width is equal to the resolution (Fig. 3), a correlation length of ~ 200 Å. In addition, the widths in the h and k directions were also resolution limited. Therefore, a new 3D long-range ordering is present with $a \times b \times 2.8c$ modulation of the structure, where c is the high conductivity direction. This could be related to a similar zero-pressure modulation reported at 24 K [2]. Attempts to measure additional peaks associated with this ordering gave ambiguous results. We attribute this both to the weak scattering from this microscopic sized sample and to the limited access to reciprocal space afforded by the diamond cell. Reduction of the pressure to 3 GPa caused this super-structure peak to disappear, Fig. 3. The expected return to 1D type scattering was not detected.

One estimate of the change in charge transfer, dz/dP , can be obtained from the Raman scattering. Our model[5] allows us to separate the two effects which cause the mode frequencies to change with pressure: the anharmonicity of the molecular potentials (often characterized by the Grüneisen parameter, γ) and dz/dP . The zero-pressure value for dz/dP is found to be about 0.02 e/GPa which is consistent with that measured for TTF-TCNQ using neutron scattering, 0.05 e/GPa [3]. Above 2 GPa indication of charge transfer are ambiguous. One Raman band shows a continuing increase at .03 e/GPa, while the other gives a decrease of .03 e/GPa. Diffuse X-ray scattering if interpreted as an ordered Peierls state gives a charge transfer of .71 at 5 GPa.

Near 4 GPa the signature of a change in the lattice translation length is found in both the Raman and X-ray scattering making it likely that the changes, in fact, occur at the same transition. While the nature of this 3D ordering is not understood it is interesting to note that the material remains highly conducting. This suggests that the modulation does not open a gap at the entire Fermi surface and points to a higher dimensionality for HMTSF-TCNQ at these pressures. Further work, especially at low temperature, is now underway in an effort to understand this behavior.

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