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# X-ray diffraction and electronic band structure study of the organic superconductor κ-(ET)₂Cu[N(CN)₂]Cl at pressures up to 28 kbar

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## Abstract

The previously observed pressure-induced amorphization transition at 11 kbar [A.J. Schultz, U. Geiser, H.H. Wang, J.M. Williams, L.W. Finger and B.M. Hazen, Physica C 208 (1993) 277] was avoided and single-crystal X-ray data up to 28 kbar were obtained by replacing mineral oil with a hydrostatic alcohol mixture as the pressure medium in a diamond anvil cell. The linear compressibilities of the crystallographic axes are remarkably isotropic given the two-dimensional nature of the structure. A full structure determination was performed at room temperature and 28 kbar with the use of X-ray data. It is noteworthy that, a novel structure feature, short *interlayer* H...H contacts through a hole in the anion layer, may account for the isotropic compressibilities. Electronic band structures calculated for the crystal structures of κ-(ET)₂Cu[N(CN)₂]Cl at 1 bar, 3 kbar and 28 kbar show that this salt is a two-dimensional metal, and that the density of states at the Fermi level decreases gradually with increasing pressure.

## 1. Introduction

The κ-phase salt of ET [ET, or BEDT-TTF, is *bis*(ethylenedithio)tetrathiafulvalene, $C_{10}H_8S_8$] (Scheme 1) with copper dicyanamide chloride, κ-(ET)₂Cu[N(CN)₂]Cl, requires a mild pressure of ~0.3 kbar to become superconducting at $T_c = 12.8$ K [2], which is the highest critical temperature for all known radical-cation based organic superconductors [3,4]. An applied stress that is sufficient for producing the superconducting state may be achieved by simply coating a crystal with vacuum grease, fol-

lowed by cooling [5]. The absence of an applied stress leads to a weakly ferromagnetic insulating state [6].

In a previous investigation of κ-(ET)₂Cu[N(CN)₂]Cl, a reversible pressure-induced structural phase transition was observed by use of X-ray diffraction at room temperature with use of a diamond anvil cell, and at low temperature by cooling grease-coated crystals [1]. In both cases, reversi-
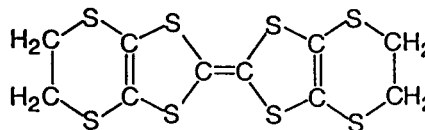
Scheme 1.

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ble broadening and splitting of the Bragg peaks occurred, suggesting a transition to a lower symmetry structure. At room temperature in the diamond anvil pressure cells, with "index of refraction" mineral oil as the hydrostatic pressure medium, a second transition characteristic of pressure-induced amorphization occurs at ~12 kbar. This transition results in the completely reversible disappearance of Bragg reflections, which reappear at lower pressures without loss of crystallinity. Another interesting finding was the isotropic character of the linear compressibilities of κ-(ET)$_2$Cu[N(CN)$_2$]Cl, which seems unusual for a layered structure of this type.

Further investigations were required to determine if the transitions described above required shear or hydrostatic pressure. This question arose since one expects the stresses from cooling a grease-coated crystal to be nonhydrostatic. This might also be the case for highly viscous mineral oil under extreme pressure in a diamond anvil cell. In this paper we describe the results obtained after replacing the mineral oil with a mixture of alcohols, which resulted in achieving pressures of up to 28 kbar *without loss* of crystallinity. We also examine the pressure dependence effects on the electronic band structures of κ-(ET)$_2$Cu[N(CN)$_2$]Cl by extended Hückel tight binding (EHTB) [7] calculations for the crystal structures at ambient pressure, 3 kbar and 28 kbar.

## 2. Experimental

### 2.1. Room-temperature diamond anvil cell X-ray data

Crystal I from our previous study [1] was removed from its diamond anvil cell and remounted with a 4:1 methanol:ethanol mixture as the pressure medium. This plate-like crystal is approximately 100 μm thick with the large flat face indexed as the (101) face. Data collection and analysis techniques were similar to those described previously [1,8]. Lattice parameters of the orthorhombic crystal, space group Pnma, were measured at 10 pressures from zero to 28 kbar by use of a new technique that fits the full peak profile to a constrained Gaussian doublet corresponding to the Kα$_1$–Kα$_2$ components of the incident X-ray spectrum. This procedure yields angles for the diffraction maxima that are free of the 2$\theta$ dependence that occurs with the previous method of locating the edges of the diffraction maxima. The results are presented in Table 1 and in Fig. 1.

The intensity measurements in the diamond anvil cell at 28 kbar were made by use of a Krisel automated Huber diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) from a conventional sealed tube X-ray source. Bragg intensities for all accessible data within a sphere of reciprocal space out to $(\sin \theta)/\lambda = 0.6$ Å$^{-1}$ were measured with use of the fixed $\phi$ mode to maximize reflection accessibility and minimize attenuation by the diamond cell [9]. Omega step scans of 0.04° increments and 8 s counting times were used.

### 2.2. X-ray data analysis

The data for each scan were converted to integrated intensities by application of the Lehman and Larson algorithm [10] except in some cases where the manual selection of backgrounds was necessary. Corrections were made for Lorentz and polarization effects, crystal absorption ($\mu = 8.989$ cm$^{-1}$) and absorption by the diamond and Be components of the pressure cell [8]. The data were also corrected for the linear decrease in intensity of the standard reflections which were measured periodically and exhibited 7% decrease at the end of the data collection. The averaging of equivalent reflections produced $R(I) = 0.037$ and $R_w(I) = 0.027$ for 539 means based on 1178 reflections ($I \gtrsim 3\sigma$). The final least-squares refinements, including corrections for anomalous dispersion and extinction ($g = 0.001(3)$ rad$^{-1}$ 10$^{-4}$) [11], are based on 702 reflections and gave $R(F) = 0.095$, $R_w(F) = 0.086$ and GOF = 2.677. All atoms are treated with isotropic thermal parameters due to the limited number of data. The atomic positional and isotropic thermal parameters are given in Table 2.

## 3. Results and discussion

### 3.1. Compressibilities and crystal structure

Measurements at pressures up to 28 kbar were performed on one of the two crystals from the previous

Table 1
Unit-cell parameters of κ-(ET)₂Cu[N(CN)₂]Cl at room temperature and several pressures

| $P$ (kbar) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å³) |
|---|---|---|---|---|
| 0.0 | 12.9681(8) | 29.925(1) | 8.4754(8) | 3289.1(4) |
| 2.6(5) | 12.8714(9) | 29.700(2) | 8.4114(5) | 3215.6(4) |
| 4.0(5) | 12.8311(6) | 29.601(3) | 8.3838(13) | 3184.3(6) |
| 7.3(5) | 12.7399(7) | 29.385(1) | 8.3281(5) | 3117.7(3) |
| 8.5(5) | 12.7006(19) | 29.286(1) | 8.3003(20) | 3087.2(7) |
| 11.0(10) | 12.6550(8) | 29.180(1) | 8.2729(7) | 3054.9(4) |
| 12.5(10) | 12.6146(10) | 29.090(2) | 8.2480(7) | 3026.6(4) |
| 14.4(5) | 12.5938(8) | 29.033(1) | 8.2339(6) | 3010.6(3) |
| 20.0(5) | 12.4963(9) | 28.800(1) | 8.1685(5) | 2939.8(3) |
| 28.0(5) | 12.4300(7) | 28.653(1) | 8.1318(4) | 2896.2(3) |
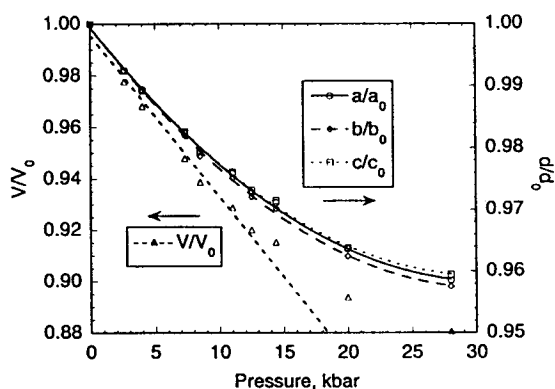


Fig. 1. Lattice constants (normalized to $P=1$ bar) vs. pressure at room temperature for κ-(ET)₂Cu[N(CN)₂]Cl. The curves for the crystallographic a-, b-, and c-axes are based on the second-order polynomial fits given in the text. The dashed line through the unit-cell volume $V$ data is a linear fit for $P \leqslant 12.5$ kbar (see text).

study, in which it had appeared to become reversibly amorphous at ~12 kbar. The only difference is that in this study the pressure medium was changed from mineral oil to a 4:1 methanol:ethanol mixture [8]. With the hydrostatic pressure medium, the Bragg peaks became sharper and more intense at higher pressure, rather than broadening and splitting.

The unit-cell parameters of κ-(ET)₂Cu[N(CN)₂]Cl at several pressures up to 28 kbar are tabulated in Table 1 and plotted in Fig. 1. The pressure dependence of the unit-cell parameters were fit to the expression

$$d = d_0 - d_1 P + d_2 P^2 ,$$

where $d_0$ is the value of the lattice parameter with zero

applied pressure, $P$ is the pressure in kbar, and $d_1$ and $d_2$ are fitted parameters. The results of this fit are

$$a = 12.961(5) - 0.0341(9)P + 0.00054(3)P^2 ,$$

$$b = 29.911(1) - 0.082(2)P + 0.00132(7)P^2 ,$$

$$c = 8.470(4) - 0.0222(7)P + 0.00036(2)P^2 .$$

The ambient-pressure linear compressibilities ($\beta = -d_1/d_0$) are $\beta_a = 2.63(8) \times 10^{-3}$, $\beta_b = 2.74(7) \times 10^{-3}$ and $\beta_c = 2.62(10) \times 10^{-3}$ kbar⁻¹. The ambient-pressure bulk modulus $K$ was calculated assuming a first-order Birch–Murnaghan equation of state with the pressure derivative $K'$ constrained to be 4 (Ref. [8], p. 160). Based on pressure–volume data to 12.5 kbar for κ-(ET)₂Cu[N(CN)₂]Cl, the bulk modulus $K$ is 124(2) kbar, which compares to a value of 122 kbar for κ-(ET)₂Cu(NCS)₂ [12]. Above 12.5 kbar, however, the pressure–volume data reveal a significant stiffening of the structure, with $K$ greater than 200 kbar. This effect occurs at the same pressure as the pressure-induced amorphization observed in the previous nonhydrostatic experiments [1], and may indicate a change in compression mechanisms at the higher pressures.

Analysis of the structure of κ-(ET)₂Cu[N(CN)₂]Cl at 28 kbar and room temperature does not reveal any qualitative changes in the packing motif or the ET molecular conformation. That is, the ethylene groups on the ET molecules retain the eclipsed conformation when viewed down the central C=C double bond of the molecule. The major changes between κ-(ET)₂Cu[N(CN)₂]Cl at 28 kbar and at lower pressures are the differences in the intermolecular contacts, which are related to the con-

Table 2
Positional and isotropic thermal parameters for κ-(ET)$_2$Cu[N(CN)$_2$]Cl at room temperature and $P=28$ kbar [a]

| Atom | $x$ | $y$ | $z$ | $U$ (Å$^2$) |
|---|---|---|---|---|
| Cu | 0.4008(4) | 0.25 | 0.5813(9) | 0.042(2) |
| Cl | 0.3790(8) | 0.25 | 0.8483(18) | 0.033(3) |
| N(0) | 0.0733(23) | 0.25 | 0.3642(57) | 0.029(10) |
| N(1) | 0.2543(25) | 0.25 | 0.4781(54) | 0.036(9) |
| N(2) | 0.0098(22) | 0.25 | 0.1013(46) | 0.005(7) |
| C(11) | 0.1720(33) | 0.25 | 0.4248(69) | 0.041(14) |
| C(12) | 0.0481(30) | 0.25 | 0.2200(75) | 0.021(11) |
| S(1) | −0.0332(5) | 0.5206(2) | 0.2715(12) | 0.028(2) |
| S(2) | 0.0906(5) | 0.5679(2) | 0.0116(12) | 0.023(2) |
| S(3) | 0.1219(5) | 0.4366(2) | 0.2739(12) | 0.029(2) |
| S(4) | 0.2556(5) | 0.4757(2) | 0.0117(13) | 0.025(2) |
| S(5) | −0.1722(6) | 0.5993(2) | 0.3470(13) | 0.034(2) |
| S(6) | −0.0220(6) | 0.6567(3) | 0.0398(13) | 0.037(2) |
| S(7) | 0.2457(6) | 0.3506(2) | 0.3112(11) | 0.028(2) |
| S(8) | 0.4031(6) | 0.3965(2) | −0.0092(13) | 0.036(2) |
| C(1) | 0.0776(18) | 0.5189(8) | 0.1421(45) | 0.023(7) |
| C(2) | 0.1452(19) | 0.4839(8) | 0.1408(47) | 0.026(7) |
| C(3) | −0.0683(18) | 0.5770(8) | 0.2202(37) | 0.025(7) |
| C(4) | −0.0129(19) | 0.5993(8) | 0.1121(40) | 0.021(7) |
| C(5) | 0.2346(19) | 0.4035(8) | 0.2134(41) | 0.022(7) |
| C(6) | 0.2915(20) | 0.4206(9) | 0.0853(41) | 0.026(8) |
| C(7) | −0.1991(22) | 0.6549(10) | 0.2430(47) | 0.054(10) |
| C(8) | −0.1082(20) | 0.6801(9) | 0.2070(43) | 0.041(9) |
| C(9) | 0.3304(19) | 0.3192(8) | 0.1672(42) | 0.030(8) |
| C(10) | 0.4301(19) | 0.3474(8) | 0.1164(41) | 0.026(8) |

[a] Temperature factors of the form $\exp(-8\pi^2 U(\sin^2\theta)/\lambda)$.

traction of the unit cell. As shown in Table 3, the S...S contacts are reduced by as much as 0.3 Å resulting in three very short distances (compared to the van der Waals sums of 3.6 Å) of S(5)...S(7) = 3.26(1), S(2)...S(5) = 3.29(1) and S(3)...S(5) = 3.31(1) Å, all involving S(5).

The highly isotropic nature of the ratios of the compressibilities, 0.96:1.0:0.96, is surprising, particularly in comparison to those for κ-(ET)$_2$Cu(NCS)$_2$, viz., 1.0:0.53:0.17 [12], which has a similar layered structure. However, the possible reason for this behavior is revealed by examination of the intermolecular H...H contacts listed in Table 3 and shown in Fig. 2. It is seen that at 28 kbar there are two such intralayer contacts of 1.99 and 2.11 Å. In addition, due to H...H contacts through holes in the anion layer, there are two interlayer contacts of 2.00 and 2.11 Å. Thus, the intermolecular ET donor–donor molecule contacts appear to be fairly isotropic, rather than two-dimensional, due to the graphs in the anion layer. It is this feature that probably accounts

for the isotropic compressibilities and that may also affect the dimensionality of the electron–phonon coupling. The reason for the anomalously high H(8A)...H(8A) distance at 3 kbar is, to some degree, indicative of the low precision of all the calculated H...H contacts, which may have esd's of 0.05 Å. The accuracy of the calculated H...H contacts are dependent on accurate C–H vectors and therefore ethylene group carbon-atom positions. In the structure determined at 3 kbar, the accuracy may have been adversely affected by the peak broadening, which at higher pressure led to amorphization, and by a precipitous 40% decrease in the intensity of the standards half-way through data collection of crystal I [1]. However, it is clear from Fig. 2 that holes in the anion layer exist and that there are short interlayer H...H contacts through those holes. There are also holes in the anion layer in the κ-(ET)$_2$Cu(NCS)$_2$ structure, but the shortest intra- and interlayer contacts at 118 K [13] are 2.18 and 3.26 Å, respectively, which is consistent with its highly anisotropic compressibili-

Table 3
Intermolecular S...S and H...H [a] contacts (Å) in κ(ET)$_2$Cu[N(CN)$_2$]Cl at room temperature and several pressures

| Atoms | $P = 1$ bar [b] | $P = 3$ kbar [c] | $P = 28$ kbar [d] | $d_{1\,bar} - d_{28\,kbar}$ |
|---|---|---|---|---|
| S(1)...S(8) | 3.598(2) | 3.57(1) | 3.38(1) | 0.22 |
| S(1)...S(4) | 3.722(2) | 3.70(1) | 3.41(1) | 0.31 |
| S(1)...S(2) | 3.740(2) | 2.71(1) | 3.50(1) | 0.24 |
| S(1)...S(4) | 3.766(2) | 3.70(1) | 3.60(1) | 0.17 |
| S(2)...S(5) | 3.615(2) | 3.58(1) | 3.29(1) | 0.33 |
| S(2)...S(3) | 3.727(2) | 3.70(1) | 3.52(1) | 0.21 |
| S(2)...S(7) | 3.796(2) | 3.73(1) | 3.50(1) | -0.30 |
| S(3)...S(5) | 3.570(2) | 3.52(1) | 3.31(1) | 0.26 |
| S(3)...S(8) | 3.784(2) | 3.73(1) | 3.52(1) | 0.26 |
| S(3)...S(4) | 3.854(2) | 3.82(1) | 3.52(1) | 0.33 |
| S(5)...S(7) | 3.489(2) | 3.44(1) | 3.26(1) | 0.23 |
| S(5)...S(8) | 3.715(2) | 3.68(1) | 3.54(1) | 0.18 |
| H(7B)...H(9B) [e] | 2.13 | 2.17 | 1.99 | 0.14 |
| H(8A)...H(8A) [f] | 2.31 | 2.56 | 2.00 | 0.31 |
| H(8B)...H(10B) [e] | 2.39 | 2.35 | 2.11 | 0.28 |
| H(9A)...H(9A) [f] | 2.59 | 2.46 | 2.11 | 0.48 |

[a] Calculated hydrogen atom positions for sp$^3$ hybridized carbon atoms with C–H = 1.09 Å.
[b] Ref. [14].
[c] Ref. [1].
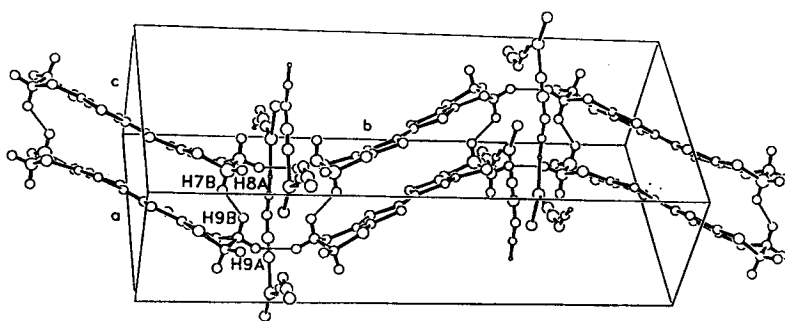[d] This work.
[e] Intralayer contact.
[f] Interlayer contact.



Fig. 2. A perspective view of a portion of the crystal structure of κ-(ET)$_2$Cu[N(CN)$_2$]Cl showing intralayer and interlayer H...H contacts ⩽2.11 Å at room temperature and 28 kbar (see Table 3). The intralayer contacts H(8B)...H(10B) are not shown. The anion layers are on crystallographic mirror planes.

ties and with the largest linear compressibility approximately along the interlayer direction.

### 3.2. Band structure

Fig. 3(a) shows the dispersion relations of the four highest occupied bands calculated for the ambient pressure structure of κ-(ET)$_2$Cu[N(CN)$_2$]Cl by employing the EHTB method. These bands are derived largely from the HOMO of each ET molecule.

With four ET$^{0.5+}$ cations per unit cell in a layer, there are six electrons per unit cell to fill the four bands so that the top two bands become partially filled. The Fermi surfaces associated with these bands (Fig. 3(b)) consist of circles, so κ-(ET)$_2$Cu[N(CN)$_2$]Cl is predicted to be a two-dimensional metal. The circles overlap along the $a^*$ direction. Our prediction that κ-(ET)$_2$Cu[N(CN)$_2$]Cl is a metal does not agree with the observation that κ-(ET)$_2$Cu[N(CN)$_2$]Cl is not a metal under ambient pressure and is only a
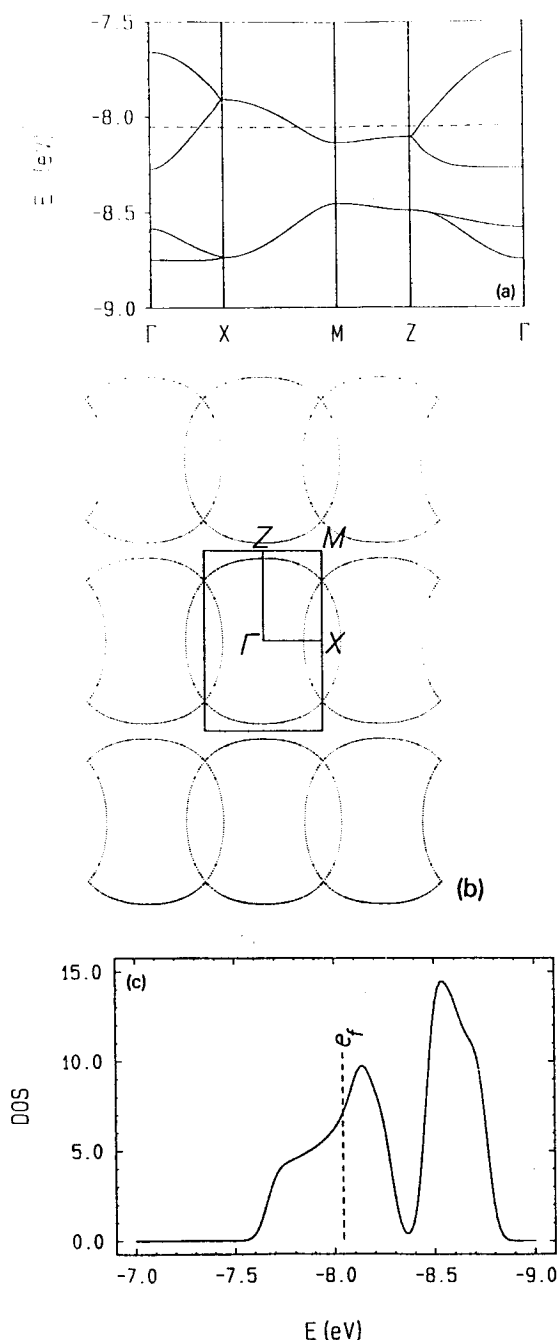
Fig. 3. Electronic structure calculated for the ambient pressure structure of κ-(ET)$_2$Cu-[N(CN)$_2$]Cl: (1) dispersion relations of the four highest occupied bands, where the dashed line refers to the Fermi level, $\Gamma = (0,0)$, $X = (a^*/2, 0)$, $Z = (0, c^*/2)$, $M = (a^*/2, c^*/2)$, (b) the Fermi surfaces associated with the partially filled bands, and (c) the density of states associated with the four bands.

metal if the sample is under applied pressure. The resolution of this inconsistency requires a proper treatment of electron correlation, which is beyond the scope of electronic band structure calculations. Fig. 3(c) shows the density of states associated with the four bands of Fig. 3(a).

The electronic band structures of κ-(ET)$_2$Cu[N(CN)$_2$]Cl calculated for the 3 and 28 kbar structures are very similar to those of the ambient pressure structure. The density of states at the Fermi level $n(e_F)$, decreases gradually with increasing pressure; the $n(e_F)$ values are 7.46, 6.97 and 5.36 electrons/eV per unit cell for the ambient-pressure, 3 kbar and 28 kbar structures, respectively. This trend is expected because the overlap between the HOMO's of the adjacent ET molecules, and hence the bandwidths, increase with decreasing the unit-cell volume under pressure. Consistent with this trend is the negative dependence of $T_c$ vs. pressure, $dT_c/dP$, after superconductivity is first observed at 0.3 kbar [2].

## 4. Conclusions

When mineral oil was used as the pressure medium in a diamond anvil cell, a reversible structural phase transition similar in appearance to the transition induced by cooling grease-coated crystals, is observed [1]. Cooling grease-coated crystals is a technique that is also used to produce the superconducting state in κ-(ET)$_2$Cu[N(CN)$_2$]Cl ($T_c = 12.8$ K, $P = 0.3$ kbar). By replacing the mineral oil in the diamond anvil cell with an isotropic pressure medium, no structural phase transition is observed up to a pressure of 28 kbar. However, from these findings we cannot conclude whether shear is necessary or, if present, simply does not interfere with the transition to a superconducting ground state.

The compressibilities of the crystal lattice are shown to be highly isotropic in nature. From an examination of the structure determined at 28 kbar, it is seen that there are short ET donor–donor molecule H...H contacts both within, and between, the ET layers through structural holes in the anion layers. These observations may also have implications with regard to the dimensionality of the electron–phonon coupling in the superconducting state.

The electronic band structures of κ-

$(ET)_2Cu[N(CN)_2]Cl$ calculated for the ambient-pressure, 3 kbar and 28 kbar crystal structures are very similar. The density of states at the Fermi level decreases gradually with increasing pressure because the unit-cell volume decreases under pressure.

## Acknowledgements

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