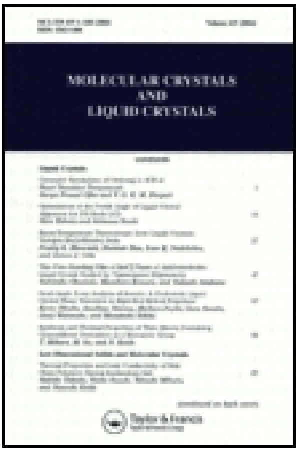
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 12:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Superelectrons from Shrunken Atoms in the Charge-Transfer Organic Compounds

M. Fukuhara [a]

[a] Technical Research Laboratory Toshiba Tungaloy 1-7, Tsukagoshi, Saiwai-Ku, Kawasaki, 210, Japan

Version of record first published: 23 Sep 2006.

To cite this article: M. Fukuhara (1995): Superelectrons from Shrunken Atoms in the Charge-Transfer Organic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 258:1, 299-314

To link to this article: http://dx.doi.org/10.1080/10587259508034570

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 299–314
Reprints available directly form the publisher
Photocopying permitted by license only

© 1995 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

Superelectrons from Shrunken Atoms in the Charge-Transfer Organic Compounds

M. FUKUHARA

Technical Research Laboratory Toshiba Tungaloy 1-7, Tsukagoshi, Saiwai-Ku, Kawasaki, 210 Japan

(Received May 3, 1994; in final form May 4, 1994)

The atomic distance between shrunken atoms in five representative organic charge-transfer superconductors, $(TMTSF)_2ClO_4$, β-$(BEDT\text{-}TTF)_2I_3$, β-$(BEDT\text{-}TTF)_2IBr_2$, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2](NCS)_2$ and K_3C_{60} were calculated and the shrunken atoms were related to T_c in comparison with inorganic superconductors. The main role of charge transfer force between the cation stack and the insulating layers of anion in the organic superconductors is a compression of the spherical inner paired electron clouds toward to the nucleus, the so-called *pintch effect*. T_c increases as the pintch effect increases. The electron pair set, $3d^{10}$ and $2p^6$, derived from the compressed atoms, Se and S, respectively, in organic superconductors can be explained as an origin of superelectrons, as well as superconducting inorganic compounds and elements.

Keywords: Superelectron, shrunken atom, pintch effect, electron pair set.

1. INTRODUCTION

We have found that there are many shrunken bonds defined as an *electronic* (or intralattice) *strain*[1,2] along the superconducting current directions in five kinds of representative inorganic superconductors, Nb_3Sn, $(La, Sr)_2CuO_4$, $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_x$ and $Tl_2Ca_2Ba_2Cu_3O_{8+x}$, and it was found that there were associated with small radius of inner closed electrons.[3] A common feature of these superconductors is the forced compression of the core electrons towards a nucleus in the superconducting atom. So we have proposed a model[1,3–5] in which superconductivity arises from pre-existing singlet pairs in filled atomic shells such as $1s^2$, $2p^6$, $3d^{10}$ and $4f^{14}$, lying below the normal conduction band. Such pairs form bosonic bands below T_c. T_c was connected to an outer electron pressure, the so-called *pintch effect*, and to the *effective potential energies* of the electron pairs, using Thomas–Fermi–Dirac (TFD) statistical method. This means that the more strongly the electron pairs bind, the higher the T_c. The linkage between the inner paired electrons was successfully explained by attractive mediation of massive photon between electron and proton.[5] The transport of the *superelectrons*[6] passing through coherent space tunnels in superconducting atoms was explained by *quantum-mechanical tunneling*. The superconducting-normal transition appears to be related to a spherical-nonspherical transition of the pair sets. Furthermore, the lattice hardening below a second-order phase transition temperature ($T_s = 117$ K), arising from volume-nonpreserving distortion, in $GdBa_2Cu_3O_{7-\delta}$ superconductor endorses this model.[7]

Our next interest lies in inquiring whether our model can also extend to organic superconductors or not. The organic superconductors (contained alkali intercalated

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

soccerball-shaped buckminster fullerene (abbreviated Bf) molecule C_{60}) studied in the past decade are all charge-transfer salts, in which there is a transfer of electric charge between organic cation and inorganic anion.[8] Although it has reported that the delocalized electrons, which are responsible for the superconductivity, come from π orbitals in the organic molecule cation,[9] it is unclear yet what mediates the attractive interaction between the electrons and what configuration the pairs are in. It is known that elements, S and Se, of the *6th* group in the organic cation of organic superconductors play an important part for electric conduction,[10] but the intrinsic role of these elements is not known, as long as we know.

For the condensation of electron pairs in organic superconductors, Choi *et al.*[11] have explained the *s*-type-singlet pairing by large critical magnetic field anisotropy, and Jérome and Schultz[12] have reported even-parity anisotropic pairing mechanism mediated by spin fluctuations near an spin-density-wave (SDW) instability in accordance with the heavy-fermion superconductors such as UP_3[13,14] and $CePb_3$.[15] Emery[16] also suggested that the pairs consist of holes on different organic stacks, using two models, exchange of SDW fluctuations and charge transfer into a second band, for the pairing force. These models are under the conventional electron-phonon based BCS theory.[17] However, in fact, the inverse of the BCS isotope effect[18] and gapless superconductivity[19] have been observed in some organic superconductors. A gapless nature in superconductivity suggests the existence of non-localized attractive force for pairing and thus puts severe constrain on the possibility of the *s*-type pairing based on the conventional BCS theory.

On the other hand, Little proposed an alternative mechanism for the formation of Cooper pairs which form by mediation of polarizing electrons, based on the polarization of side molecules attached to a spine of carbon atoms.[20] No one, however, has yet succeeded in building such a molecule having the properties Little envisioned, although Little's idea had stimulated strong interest in the development of organic superconductors.

In this paper, the bonding distances between superconducting atoms in three representative organic charge-transfer superconductors, the Bechgaardditetra-methyltetraselenaful-valence salts (TMTSF, $C_5H_6Se_2)_2X$ ($X = PF_6$,[21] AsF_6,[22] ClO_4[23]...); *i.e.*, Bechgaard salts,[24] bis(ethylenedithia)tetrathiafulvalene (BEDT-TTF, $C_{10}H_8S_8$, or abbreviated $ET)_2Y$ ($Y = ReO_4$,[25] I_3,[26] $Cu(SCN)_2$,[27] $Cu[N(CN)_2]Br$,[28] $Cu[N(CN)_2]Cl$[29]...) and the fullerides, A_xC_{60}, intercalated with alkali metal atoms such as A = K,[30] Rb[31] and Cs[32] are calculated and compared with those of Van der Walls and organic radii, as wall as the intralattice strain analysis in the previous paper.[1] Using the fractional change in the interatomic distance found in the structure with reference to the normal radii as an intralattice (or electronic) strain, effective potential energies of the electron pairs and the compressive pressure of outer electrons are investigated on the basis of the TFD method, as well as in the previous paper.[3]

CALCULATION OF BONDING DISTANCE

The atomic distance of two metals in complex was calculated as the sum of the Van der Waals radii by Bondi.[33] The single bond length between C and S atoms in the five and six membered rings of $(ET)_2Cu(SCN)_2$ was taken from a shortened bond distance, 0.173 nm in the International Table.[34] The atomic distance between C and K atoms in K_3C_{60} molecules was calculated as the respective sums of the interatomic radii of C and K atoms, using metallic radius 0.236 nm for K[35] and C—C bond distance, 0.1545 nm, in diamond.[34] The length of double C—C bond which holds in common two six membered rings in $(ET)_2Cu(SCN)_2$ and C_{60} molecules was taken from the partial double C—C bond length, 0.1395 nm,[34] of the aromatic compound. The single bond length, 0.153 nm,[34] shortened in presence of aromatic ring, was used as an interatomic distance of C—C single bond which composes five membered rings in the $(ET)_2$ $Cu(SCN)_2$ and C_{60} molecules.

In order to give careful calculation to the interdistance radii, another method, the bond valence calculation method,[36,37] also must adopt as well as in the previous paper.[1] However, since the method uses a relatively rough hypothesis, that the valence distribution is uniform, it is difficult to use it for these charge-transfer salts with irregular coordination figures.

BONDING DISTANCES IN THE SUPERCONDUCTING COMPOUNDS

(TMTSF)$_2$X System

The first organic superconductor, $(TMTSF)_2PF_6(T_c = 0.9)$ was discovered under pressure of 12 kbar by D. Jérome *et al.*[38] Since then they have found superconductivity in crystals of $TMTSF_2X$ made from hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), hexafluorotantallate (TaF_6^-), perrhenate (ReO_4^-), and perchlorate (ClO_4^-),[39] where TMTSF is an organic cation positively charged and X is an inorganic anion negatively charged. All these Bechgaard salts except for $(TMTSF)_2ClO_4$ are stress-induced superconductors, but $(TMTSF)_2ClO_4$ becomes superconductive at 1.2 K and ambient pressure.[40] TMTSF are quasi-planar dimerized molecules stacked in a zigzag pattern along the *a*-axis. The Bechgaard salts are isostructural, with only small difference in lattice parameters related to the sizes of the anions, so a crystal structure (Figure 1) of triclinic $(TMTSF)_2ClO_4$ at 7 K[41] is selected as a representative

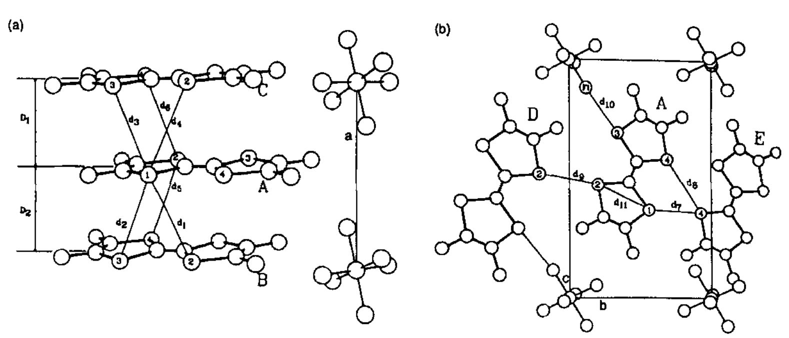


FIGURE 1 Molecular stacking in $(TMTSF)_2Cl_4$; side-view (a) and view (b) along *a* axis showing intermolecular interstack Se—Se contact distances.[45]

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

example of the $(\mathrm{TMTSF})_2\mathrm{X}$ type structures. Indeed, to the author's knowledge, the crystal structures with other anions are not analyzed at low temperature near T_c.

The structure of $(\mathrm{TMTSF})_2\ \mathrm{ClO_4}$ is characterized by the shorter Se—Se distances; the interplanar spacing (stack) of the nearly planar TMTSF molecules are linked by short intermolecular Se—Se contacts, both along the stacking direction (the *a* axis) and normal to the stacks (along *b*). The atomic bonding distances between Se atoms are presented in Table 1, together with Van der Waals Se—Se bond distance. Intramolecular Se—Se distance (d_{11}) was taken from the data 0.3150 nm at 298 K,[42] because there is no available data at low temperature. The shorter Se—Se distance within a stack (d_1 to d_6) are longer than the sum of the Van der Waals radii for Se (0.38 nm), while two of the shorter interchain Se—Se distances (d_7 and d_9) are shorter than that of the sum. In other words, Se atoms along the *b* axis are remarkably forced to shrink. However, the S—S contacts are not continuous along the *c*-axis, because of existence of the $\mathrm{ClO_4}$ anions. Lattice parameter temperature dependence reveals abrupt decrease of the *a* parameter (0.724 to 0.707 nm) and γ value ($70.6\pi/180$ to $69.0\pi/180$ rad) as the temperature decreases from 295 K[23] to 719.[41] The further structure analysis at low temperature below T_c will make all the shrinkage percentages increase still more.

These results suggest accumulation of intralattice strain, as well as T_c *vs* rhombicity relation in cuprate oxide superconductors with rhombohedral structure.[1] This may be

TABLE I

Atomic bonding distances among Se and C atoms in $(\mathrm{TMTSF})_2\mathrm{ClO_4}$ at 7 K[41]

Bonding distance A (nm) Interatomic distance B (nm)	Bonding direction	Percent shrinkage $\frac{A-B}{A}\times 100$ (%)
$d_3 \quad d_2$ $\mathrm{Se_3}\frac{0.289}{0.38}\mathrm{Se_1}\frac{0.382}{0.38}\mathrm{Se_3}$	*a* axis	$(-23.95)-(+0.53)$
$d_3 \quad d_1$ $\mathrm{Se_3}\frac{0.289}{0.38}\mathrm{Se_1}\frac{0.408}{0.38}\mathrm{Se_2}$	*a* axis	$(-23.95)-(+7.37)$
$d_6 \quad d_5$ $\mathrm{Se_4}\frac{0.383}{0.38}\mathrm{Se_2}\frac{0.386}{0.38}\mathrm{Se_4}$	*a* axis	$(+0.79)-(+1.58)$
$d_4 \quad d_2$ $\mathrm{Se_2}\frac{0.396}{0.38}\mathrm{Se_1}\frac{0.382}{0.38}\mathrm{Se_3}$	*a* axis	$(+4.21)-(+0.53)$
$d_4 \quad d_1$ $\mathrm{Se_2}\frac{0.396}{0.38}\mathrm{Se_1}\frac{0.408}{0.38}\mathrm{Se_2}$	*a* axis	$(+4.21)-(+7.37)$
$d_9 \quad d_{11} \quad d_7$ $\mathrm{Se_2}\frac{0.357}{0.38}\mathrm{Se_2}\frac{0.315}{0.38}\mathrm{Se_1}\frac{0.372}{0.38}\mathrm{Se_4}$	*b* axis	$(-6.05)-(-17.11)-(-2.11)$

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

related to the superconductivity in Bechgaard salts, as it does between metal atoms in inorganic compound superconductors.[1,4] The superconducting current will be predominant on the *ab* plane. These discussions agree favorably with the diamagnetic data for single crystal.[43] Since T_c is determined by one minimum shrinkage ratio in this bond series, the shrinkage ratio (-2.11%) of the S—S bond would be the critical factor determining T_c.

If the electron pair itinerates from the compacted Se atoms as the origin of superelectrons, as can be deduced from the previous paper,[3] superelectrons would be $3d^{10}$ electron pairs with spin-singlet pairing, corresponding to the Russel–Saunders term symbol $^1S_0$. The fivefold degenerated electron pair set behaves as the *s*-type spin-singlet pair, because the superposition of five *d*-electron pair clouds gives a spherical charge distribution in space-time. In contrast, Schultz[44] had suggested that there is a spin anisotropic triplet superconducting states in quasi-one-dimensional conductors.

Since all the derivatives $(TMTSF)_2X$ ($X = AsF_2$, BrO_4, PF_6, ReO_4 and FSO_3) superconductors have larger Se—Se distances at 125 K[45] compared with that of $(TMTSF)_2ClO_4$, they require an applied pressure of ~ 8–12 kbar to induce the superconducting state.[46] Compression will serve decreasing of the *b* axis. T_c would increase further if the intrastack distances draw near the interplanar one (D_1 or D_2). In $(TMTSF)_2$ ClO_4, thus, ordered ClO_4^- anions in the lattice hole seems to play a similar role for compression of the TMTSF stack, because the role of the anion is to systematically contract or expand the Se—Se "sheet network" in a predictable manner.[47] Indeed, the ClO_4^- anion as well as ReO_4^-, which are non-centrosymmetric in the hole,[48] orders along alternative direction below order-disorder temperature T_{od} (= 24 K[49]).

(BEDT-TTF)$_2$Y System

Since 1983, when Parkin *et al.*[25] found $(ET)_2ReO_4$ to be superconducting below about 2.5 K, the highest critical temperatures among ordinary organic superconductors have been found in salts of the form $(ET)_2Y$. Kini *et al.*[28] discovered the bromine salt κ-$(ET)_2Cu[N(CN)_2]Br$ which becomes superconducting at 11.6 K and ambient pressure, and William *et al.*[29] found the clorine salt κ-$(ET)_2Cu[N(CN)_2]Cl$ which is a superconductor below 12.8 K under a pressure of 0.3 kbar. Superconducting ET salts is mainly divided into categories, i.e, β-and κ-phases. The β-phase salt consists of an isostructural series of salts with linear, triatomic anions such as I_3^- ($T_c = 1.4$ K at ambient pressure,[26] 8 K at 0.5 kbar[50]), IBr_2^-($T_c = 2.8$ K at ambient pressure [51]) and AuI_2^- ($T_c = 4.8$ K at ambient pressure[52]). All κ-phases salts have face-to-face molecular dimers, which are oriented approximately at right angles with respect to their neighbors, forming a two dimensional S···S network. Since we have only two crystal structure data reported for $(ET)_2Y$ system at low temperature near T_c, as far as we know, the β-$(ET)_2I_3$ with $T_c = 1.4$ K[26] and the κ-$(ET)_2Cu(NCS)_2$ salt with $T_c = 10.4$ K[53] are thus selected as two representative examples of $(ET)_2Y$ structure in this section.

The β-$(ET)_2I_3$ *salt.*

The crystal structure (Figure 2) was determined from neutron diffraction data at 4.5 K by Schultz *et al.*[54] Since both a lattice parameter of *b*-axis and α value at 1.5 kbar

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

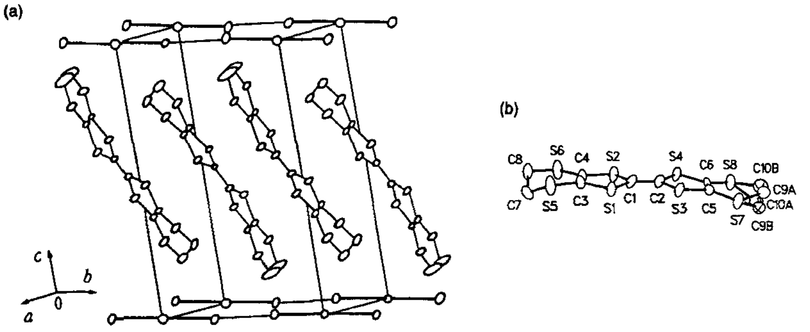


FIGURE 2 The three dimensional view (a) of β-$(ET)_2I_3$ structure and ET molecule (b) along *c* axis.[54]

abnormaly depart from smooth curves in lattice parameters of *a* and *c* axis, and in β and γ values, it is not clear whether the sample analyzed at 4.5 K and 1.5 kbar shows transition temperature of 8 K or not, although it is reported by other research groups[50] that the pressure-induced structural transition from the modulated β-$(ET)_2I_3$ to the completely ordered β^*-$(ET)_2I_3$ produces a dramatic rise in T_c to 8 K. Thus we regard the data analyzed at 1.5 kbar as the ambient pressure data of β-$(ET)_2I_3$ salt with $T_c = 1.4$ K.[26] The structure is triclinic with two ET molecules per unit cell. The ET cation radicals are packed in the crystal plane-to-plane with the centrosymmetrical linear I_3^- anions. The staggered cation molecular stacks in the crystal are related to each other by symmetry operations. Since the percent shrinkages of shrunken bonds among S and C atoms are generally larger than those of the bonds between S ones, the atomic bonding distances between S atoms are presented in Table 2. It should be noted that the interstack distances S ⋯ S, which are smaller than all S ⋯ S distances in the intrastacks, provide the electron conduction pathways.[55]

TABLE II

Atomic bonding distances among S atoms in β-$(BEDT\text{-}TTF)_2I_3$ at 45 K and 1.5 kbar.[54] Superscripts refer to symmetry operations: (1) $-x, -y, 1-z$; (2) $-x, -1-y, 1-z$; (3) $1+x, y, z$; (4) $-1+x, y, z$; (5) $1-x, -1-y, 1-z$

S—S Contact	Bonding distance *A* (nm)	Interatomic distance *B* (nm)	Percent shrinkage $\frac{A-B}{A} \times 100$ (%)
S_1—S_4^{2}	0.3643	0.36	+1.19
S_1—S_4^{3}	0.3671	0.36	+1.97
S_2—S_3^{2}	0.3640	0.36	+1.11
S_2—S_5^{4}	0.3538	0.36	−1.72
S_3—S_4^{2}	0.3646	0.36	+1.28
S_3—S_8^{3}	0.3526	0.36	−2.06
S_4—S_6^{1}	0.3610	0.36	+0.28
S_5—S_6^{3}	0.3451	0.36	−4.14
S_5—S_7^{5}	0.3480	0.36	−3.33
S_6—S_8^{1}	0.3548	0.36	−1.44
S_7—S_8^{3}	0.3420	0.36	−5.00

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

The lattice parameters of the *a*, *b* and *c* axis and unit cell volume, and α, β and γ values considerably decrease and increase, respectively, as temperature decrease from 298 to 4.5 K,[54] suggesting accumulation of intrastrain at low temperature. If these bonds are related to superconductivity as has been suggested for the $TMTSF_2X$, the current on the *ab* plane will be predominant. In fact, the β-$(ET)_2I_3$ is a two-dimensional metal along the *ab*-plane.[26,55] The shortest bond, S_7—S_8, which is 0.342 nm, would be a conduction pathway determining T_c. Superelectrons derived from S would be $2p^6$ electron pairs with the Russel–Saunders state $^1S_0$.[3] The threefold degenerated *p*-electron pair set also acts as *s*-type spin-singlet pair. A lattice parameter of *b* axis would decrease further if the sample is analyzed at 8 K and 0.5 kbar.

Furthermore, we consider another ambient pressure superconductor β-$(ET)_2$ IBr_2 with $T_c = 2.8$ K.[56] Since the ET molecular structure of β-$(ET)_2Y$ salts has similar features, we compare inter-and intrastack S—S distances of two β-$(ET)_2Y$ salts, using the data analyzed at 120 K by Emge *et al.*[57] At 120 K, all the S···S contacts for β-$(ET)_2IBr_2$ are shorter than those for β-$(ET)_2I_3$, suggesting higher T_c in β-$(ET)_2IBr_2$ compared with β-$(ET)_2I_3$. In fact, T_c of the former is higher than that of the latter. However, discussions about the former must be limited at present, because of no available data for crystal analysis below T_c.

The κ-$(ET)_2Cu(NCS)_2$

The structure (Figure 3) was determined at 15 K by Schultz *et al.*[58] and analyzed by H. Mori.[59] Two ET donor molecules in κ-$(ET)_2Cu(NCS)_2$ form a dimerized pair which are linked to one another almost perpendicularly to construct a two-dimensional conducting sheet in the *bc*-plane. Every layer is sandwiched by insulating layers of anion along the *a*-axis.[19] The structure is characterized by the staggered ET molecule conformation and several short intra-and inter-pair S···S contacts. Since the percent shrinkages of shrunken bonds among S and C atoms are generally larger than those of the bonds between S ones, as well as in β-$(ET)_2I_3$ salts, the atomic bonding distances between S atoms are presented in Table 3.

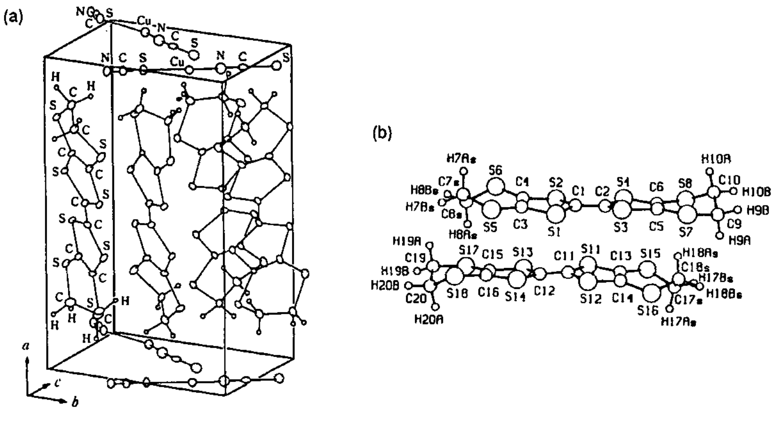


FIGURE 3 The three dimensional view of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2](NCS)_2$ structure[53] and the ET dimers with staggered conformation.[58]

TABLE III

Atomic bonding distances among S atoms in β-(BEDT-TTF)$_2$Cu (NCS)$_2$ at 15 K[58]

S—S Contact	Bonding distance A (nm)	Interatomic distance B (nm)	Percent shrinkage $\frac{A-B}{A} \times 100$ (%)
S_1—S_8	0.329494	0.36	−8.47
S_1—S_{11}	0.171278	0.36	−52.42
S_1—S_{13}	0.196342	0.36	−45.42
S_2—S_7	0.326651	0.36	−9.26
S_2—S_8	0.335655	0.36	−6.76
S_2—S_{11}	0.305766	0.36	−15.07
S_2—S_{13}	0.320285	0.36	−11.03
S_3—S_2	0.358374	0.36	−0.45
S_3—S_4	0.309992	0.36	−13.89
S_3—S_{11}	0.201872	0.36	−43.92
S_3—S_{15}	0.141738	0.36	−60.63
S_4—S_4	0.326108	0.36	−9.44
S_4—S_{11}	0.313242	0.36	−12.99
S_4—S_{15}	0.308817	0.36	−14.22
S_5—S_{13}	0.176769	0.36	−50.90
S_5—S_{17}	0.200473	0.36	−44.31
S_6—S_{13}	0.331587	0.36	−7.89
S_6—S_{17}	0.332970	0.36	−7.51
S_7—S_{15}	0.182811	0.36	−49.22
S_8—S_{15}	0.349554	0.36	−2.90

The lattice parameter of the c-axis and unit cell volume considerably decrease from 1.312 to 1.278 nm and from 1.688 to 1.630 nm^3, respectively, and β value increases from $110.30\pi/180$ to $111.45\pi/180$ rad as temperature decreases from 298 to 15 K,[53,58] suggesting accumulation of intrastrain at low temperature. If these bonds are related to superconductivity as has been suggested for the TMTSF$_2$X, the current on the bc plane will be predominant. In fact, the κ-(ET)$_2$Cu[N(CN)$_2$] (NCS)$_2$ is a two-dimensional metal along the bc-plane.[60] The shortest bond, S_3—S_{15} which is 0.1417 nm, would be a conduction pathway determining T_c. Superelectrons derived from S would be $2p^6$ electron pairs, as well as in β-(ET)$_2$I$_3$ salt.

For another κ-phase salt, Watanabe *et al.*[61] have determined lattice parameters of κ-(ET)$_2$Cu[N(CN)$_2$]Br down to 20 K, but not analyzed the atomic structure. Therefore, discussions about the κ-(ET)$_2$Cu[N(CN)$_2$]Br salt are limited.

AxBf System

The pseudosphere of fulleride C_{60} is covalently bonded, but when it is intercalated with alkali atoms, electrons are transferred to the Bf cage, resulting in an ionically bonded solid AxBf, namely charge-transfer salt[62] and then the material becomes superconducting below T_c of 18 K, 28 K, 30 K and 33 K for A = K,[30] Rb,[31] Cs[32] and Cs$_2$Rb,[63] respectively. A face-centered cubic K_3C_{60} with $T_c = 19.3$ K is selected as a representative example of the AxBf system. We used the crystal structure which determined at room temperature by Stephens *et al.*,[64] because the data in low temperature regions

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

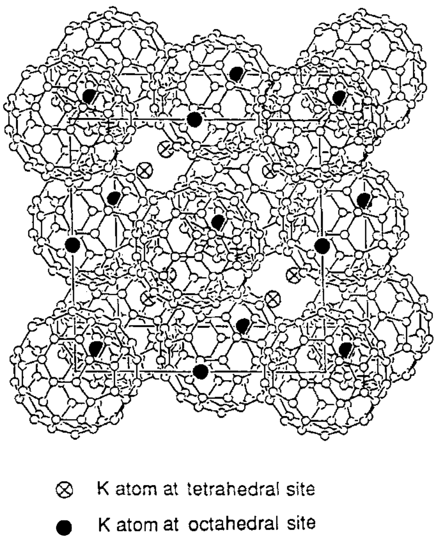


FIGURE 4 The fcc lattice structure of K_3C_{60}. Open circles represent carbon atoms of the Bf cage.

has not been reported up till now. In this structure (Figure 4), C_{60} molecules are surrounded by eight K^{t+} at the center of the tetrahedron consisting of four nearest-neighbor C_{60}, and six K^{o+} located at the middle of every two next-nearest-neighbor C_{60}. Table 4 shows the atomic distances between C atom of the Bf cage and K atom, inserted at octahedral and tetrahedral sites in the fcc lattice, and between the C—C bonds along the cage.

Shrinkage of the nearest-neighbor C—K^t distance, separating the potasium atom at tetrahedral site from the six membered carbon rings directly facing them in each of four C_{60} molecules, is smaller than that of the nearest-neighbor C—K^o distance from the octahedral K^o site to the nearest C atom. We can thus visualize a continuous zigzag shrunken bond, —K^t—C_{60}—K^t—, along [100], [110] and [111] directions in the K_3C_{60} lattice. Occupation of potasium atoms at the tetrahedral sites facilitates accumulation of strain, accompanied by shrinkage of the carbon radius. If these shrunken bonds are related to superconductivity as has been suggested for the salts mentioned above, the almost three dimensional current along these directions will be predominant. The percentage shrinkage of all atoms will increase still more if the crystal structure is determined at low temperature below T_c. In fact, since the lattice constant of the fcc C_{60} decreases from 1.424 to 1.4043 nm as the temperature decreases from room temperature to 15 K,[65] all data in Table 4 expect to decrease still more at low temperature below T_c. However, discussions about the K_3C_{60} must be limited up till the crystal data below T_c will report.

In addition, it would be desirable for the occurrence of superconductivity to occupy alkali atoms with large radius into the tetrahedral sites without disrupting the close-packing. Indeed, T_c of the AxBf compounds increases monotonically as the radius of the alkali atom increases.[66] This means increase in strain, because expansion rate of

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

TABLE IV

Atomic bonding distances among K and C atoms in K_3C_{60} at room temperature. K^t and K^o denote K atom inserted at tetrahedral and octahedral sites, respectively at room temperature; C—C is single bond which composes five membered rings and C=C is double bond which holds in common two six membered rings

Bonding distance A (nm) / Interatomic distance B (nm)	Bonding direction	Percent shrinkage $\frac{A-B}{A} \times 100$ (%)
$\mathrm{K}^t\overset{0.266}{\underset{0.313}{\text{——}}}\mathrm{C}\overset{0.1348}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1595}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{K}^t$	[100]	$(-15.07)-(-3.37)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-(-15.07)$-
$\mathrm{K}^t\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{K}^t$	[010]	$(-15.07)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-(-4.90)-(-15.07)$
$\mathrm{K}^t\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{K}^t$	[110]	$(-15.07)-(-3.37)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-(-4.90)-(-15.07)$
$\mathrm{K}^t\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}$ $\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.112}{\underset{0.313}{\text{——}}}\mathrm{K}^t$	[111]	$(-15.07)-(-3.37)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-(-4.90)-(-3.37)-$ $(-4.90)-(-15.07)$
$\mathrm{K}^o\overset{0.369}{\underset{0.313}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.1391}{\underset{0.1395}{==}}\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}$ $\mathrm{C}\overset{0.1455}{\underset{0.153}{\text{——}}}\mathrm{C}\overset{0.369}{\underset{0.313}{\text{——}}}\mathrm{K}^o$	[111]	$(+17.89)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-(-4.90)-(-3.37)-(-4.90)-$ $(-4.90)-(+17.89)-$

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

the atomic radius from K to Cs is ten times as large as that of the corresponding unit cell size. The charge transfer force in this charge-transfer K_3C_{60} compound will serve considerable shrinkage of potassium and carbon atoms.

DISCUSSION

Although normal conductivity anisotropy along the *a* axis in the $(TMTSF)_2X$ system and the *bc*-plane in the $(ET)_2Y$ system, and three dimensional normal conductivity in AxBf are explained by orbital overlap of π (outer *p*) electron wavefunctions in sulfur or selenium atoms that are made neighbors by the stacking,[10] it is unclear yet how these electrons make pair and where the conduction pathway for superelectron in the compounds lies.

Both S and Se atoms which compose heterocycles in the organic charge-transfer superconductors are elements of the *6th* group as well as O atoms in oxide superconductors, but the formers seem to play an important part in superelectron conduction in contrast with the latter's role served as relief of repulsive force between electrons.[1,5] Since it is considered that superelectrons derived from the shrunken Se and S atoms in $(TMTSF)_2X$ and $(ET)_2Y$ compounds are $3d^{10}$ and $2p^6$ electron pairs, respectively, the effective potential energies of the degenerated electrons in a spherical-field orbital are calculated by using the TFD method[6,7] described in the previous paper.[3] These energy values are plotted as a function of T_c in Figure 5, together with the potential energy connected with the atoms of four inorganic ones in the previous paper,[5] because there are similarities between organic and oxide superconductors such as their low electron densities, two dimensionality and optical inelastic scattering rate for electrons that varies linearly with the frequency or the temperature. As the energy V increase, T_c increases as

$$T_c = -2.4515 - 0.1279V - 2.7238 \times 10^{-4} V^2 - 9.7811 \times 10^{-7} V^3 \qquad (1)$$

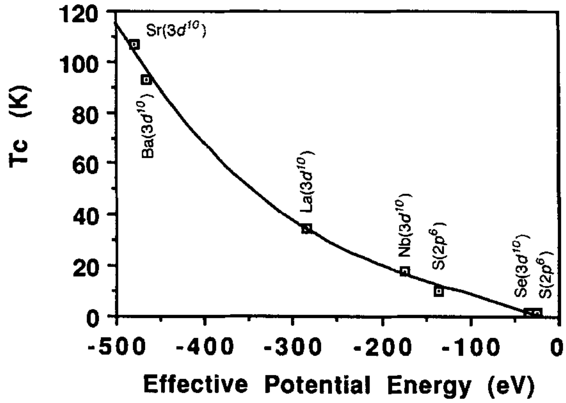


FIGURE 5 Relation between T_c and effective potential energy of paired electrons in seven kinds of superconductors, $(TMTSF)_2Cl_4$ ($T_c = 1.2$ K), β-$(BEDT\text{-}TTF)_2I_3$, ($T_c = 1.4$ K), κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2](NCS)_2$ ($T_c = 10.4$ K), K_3C_{60}($T_c = 19.3$ K), Nb_3Sn ($T_c = 18.05$ K), $(La, Sr)_2CuO_4$ ($T_c = 35$ K), $YBa_2Cu_3O_{7-\delta}$ ($T_c = 93$ K) and $Bi_2Sr_2CaCu_2O_x$ ($T_c = 107$ K).

Eq. (1) means that the more the attractive interaction, that is, more the binder energy increases, the higher T_c increases. Therefore, it is expected that the potential energy of the degenerated electrons in K_3C_{60} with $T_c = 19.3$ K would be -189 eV. Assumed from the TFD calculation, the corresponding electron radius of the shrunken atom is 2.1 and 6.4 nm for carbon atom with $1s^2$ electrons and potasium one with $2p^6$ ones, respectively. Since it is extremely difficult for carbon atoms in the Bf cage to shrink down to 2.1 nm as temperature decreases from room temperature to T_c, superelectrons derived from K_3C_{60} would be s-type $2p^6$ electrons in potasium atom, as can be assumed from previous paper.[3] However, we cannot determine the conduction pathway of superelectrons in C_{60}, because of no available data for crystal structure analyzed at temperature below T_c. T_c of carbon compound superconductors with $2p^6$ electron pairs substantially increase from 0.020 K in the Cs intercalated graphite compound[68] to 45 K in Rb/Tl codoped C_{60} and C_{60}/C_{70} mixtures[69] as carbon radius decreases.

Next we calculate the compressive pressure due to outer electrons, on the basis of the TFD model as well as the previous paper.[3] The relation between the shell compressive pressure P (GPa) and T_c is expressed in Figure 6, where T_c can be expressed as

$$T_c = -2.0645 - 12.7290P - 1.3601\,P^2 + 0.06369P^3 \tag{2}$$

The role of the outer electrons is thus an application of large compression against the spherical paired electron clouds around the nucleus due to the pintch effect.

As the shrinkage mechanism for organic superconductors, we can visualize two models; one is a hydrogen bond model and the other is an electrostatic force one by charge transfer. It is probably the latter, because of no existence of hydrogen bond in the AxBf compounds. It is recognized that all the charge-transfer complex at room temperature are formed by a weak interaction of electron donors with electron acceptors.[70] However there is no available data for the charge transfer force below T_c. As assumed from abrupt decrease of the a parameter and γ value of the $(TMTSF)_2X$ system, and the c-axis and unit cell volume of the $(ET)_2Y$ system in low temperature

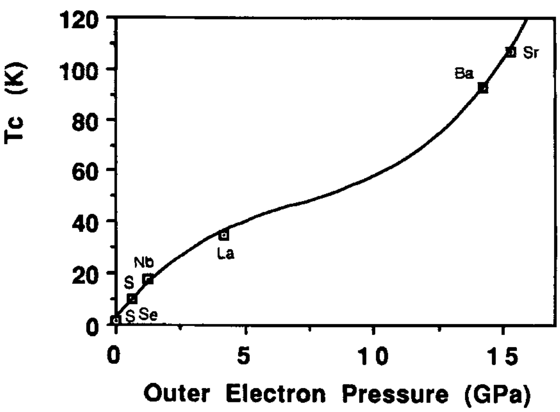


FIGURE 6 Relation between T_c and the subjective compression pressure against the spherical closed shell in seven kinds of superconductors.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

range, the force seems to increase remarkably due to augmentation of attractive interaction between the cation stack and the anion, as the temperature decreases. Then we consider enhancement of the force in the low temperature range.

The force between the donor and the acceptor molecules has been explained by two models, *valence-bond (resonance)*[71] and *free electron*[72] ones.[73] The latter model by Shuler[74] and Boeyens[75] treats the π-electrons in a conjugated molecule as a free electron gas which moves in the potential field of the molecule. The model is a convenient description for correlating the experimentally observed effects of pressure on the charge-transfer complexes, because the shortening of the intermolecular distance can be directly related to the width of the potential barrier and hence to the probability of tunneling through the smaller potential barrier.[74]

Since the barrier width and height decrease still more when temperature decreases, the mobile π-electrons can tunnel more easily through the smaller potential barrier in the complex. The attractive force F acting between two molecules can be thus described as follows:

$$F(r,T) = -\frac{\alpha\mu_A{}^2\mu_B{}^2}{r^6}e^{-V/k_BT}, \tag{3}$$

where μ_A and μ_B are permanent electric dipole moments of the molecules A and B, respectively, r is an intermolecular separation, α constant and k_B Boltzman constant. The attractive force can be also represented in the form, using a quantum mechanical perturbation theory,[76]

$$F(T) = \frac{2\beta^2}{\varepsilon_{LUMO}(T) - \varepsilon_{HOMO}(T)}, \tag{4}$$

where ε_{LUMO} and ε_{HOMO} are orbital energies of LUMO and HOMO, respectively, and β is exchange interaction energy of both orbitals, $\langle$HOMO |H| LUMO$\rangle$. The stability of the complex AB increases with increasing delocalization of the π-electrons. Thus decrease in temperature facilitates the charge transfer force which serves as the pintch effect. Decrease of the electron–electron Coulomb repulsion in this complex can be explained by the screening effect due to the condensed electron, as well as the cuprate oxides in the previous paper.[4] For the gapless nature in superconductivity described above, the non-localized force and the space symmetry can be well explained, using our theory[1–5] which is mediated by the nucleus with large positive charge.

Furthermore, as can be expected from theoretical treatment by Shuler[74] and Boeyens,[75] an effect of hydrostatic pressure on condensation of molecules A and B is larger in intermolecular changes rather than in intramolecular ones. Especially this effect results in reduction of the equilibrium intermolecular distance, as well as effect of decreased temperature. However, in practice, the negative pressure dependence of T_c has been observed in the following superconductors, β-$(ET)_2Y$ salts,[77]κ-$(ET)_2Cu(NCS)_2$[78] and K_3C_{60}.[79] Kini *et al.*[28] have reported that the pressure dependence suggests the expansion of the ET donor molecule network, attainable through the incorporation of even larger polymeric anion. Here, it should be noted that intermolecular O–O distance in high-pressure phase of ice, which is a kind of the charged-transfer salt, increased from 0.276 nm in ice I at 0.1 MPa to 0.286 nm in ice VII at 2.5 GPa, accompanying by change of an included angle of H—O—H,[80] due to

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

positive repulsion between protons in hydrogen bond, O—H...O. Hence, by analogy we infer that the negative pressure effect in these charge transfer superconductors shows the stress-induced repulsion between protons in the included angle of H—S—H or H—N—H.

In this study, superconductivity of organic charge-transfer superconductors can successfully be explained in connection with maximum shrinkage ratio of atoms such as Se and S in shrunken bond pathways. Thus our theory, which was proposed in superconducting elements and inorganic compounds, can also extended to organic superconductors. The mobile π-electrons make energetically favorable for the charge-transfer complex to condense in the region of the low temperature. The main role of the charge-transfer force between the cation stack and the insulating layers of anion is a compression of the spherical paired electrons in superconducting atoms toward to the nucleus due to the pintch effect. In a subsequent paper, we will address problem why superconducting substances suddenly become nonsuperconductive at a special temperature; attention will be given to the dynamical interaction between massive photon and nucleons at T_c.

References

1. M. Fukuhara and H. A. McKinstry, *Phys. Stat. Sol.* (*b*), **157**, 357 (1990).
2. M. Fukhara, A. S. Bhalla, R. E. Newnham, L. E. Cross and R. Roy, *Mater. Letters*, **6**, 398 (1988); M. Fukuhara, A. S. Bhalla, L. N. Mulay and R. E. Newnham, *J. Mater. Res.*, **4**, 273 (1989).
3. M. Fukuhara, *Phys. Stat. Sol.* (*b*), **175**, 421 (1993).
4. M. Fukuhara and G. W. Smith II, *Phys. Stat. Sol.* (*b*), **156**, 583 (1989); M. Fukuhara, *Trans. Mater. Sci. Japan*, **2**, 59 (1992).
5. M. Fukuhara, unpublished.
6. A *superelectron* is defined as the coupled electron pair with twice the charge and mass of an electron: A. C. Rose–Inness and E. H. Rhoderick, *Introduction to Superconductivity*, Pergamon Press, (1978), p. 138; U. Essmann and H. Träuble, *Sci. Amer.*, **224** (3), 75 (1971).
7. M. Fukuhara and A. Sanpei, *Phys. Rev.*, **B49** (18), 13099 (1994).
8. A. Khurana, *Phys. Today*, **15** (12), 17 (1990).
9. P. M. Chaikin and R. L. Greene, *Phys. Today*, **May**, 24 (1986).
10. F. Wudl, *J. Am. Chem. Soc.*, **103**, 7064 (1981).
11. M. -Y. Choi, P. M. Chaikin, P. Haen and R. L. Greene, *Solid State Commun.*, **41**, 225 (1982).
12. D. Jérome and H. Schulz, *Adv. Phys.*, **31**, 299 (1982).
13. G. Aeppli, A. Goldman, G. Shirane, E. Bucher and M. -Ch. Lux-Steiner, *Phys. Rev Lett.* **58** (8), 808 (1987); D. J. Scalapino, E. Loh, Jr and J. E. Hirch, *Phys. Rev.*, **B34** (11), 8190 (1986).
14. J. E. Hirsch, *Phys. Lett.*, **54** (12), 1317 (1985); M. T. Béal–Monod, C. Bourbonnais and V. J. Emery, *Phys. Rev.*, **B34** (11), 7716 (1986).
15. C. L. Lin, J., Teter, J. E. Crow, T. Mihalisin, J. Brooks, *Phys. Rev. Lett.*, **54** (23), 2541 (1985).
16. V. J. Emery, *Synthetic Metals*, **13**, 21 (1986).
17. J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, **108** (5), 1175 (1957).
18. C. P. Heidmann, K. Andrew and D. Schweitzer, *Physca*, **143B**, 357 (1986); G. Saito, H. Urayama, H. Yamochi and K. Oshima, Synthetic Metals, **27**, A331 (1988).
19. K. Kanoda, T. Takahashi and G. Saito, *Physica C*, **162**, 405 (1989); K. Kanoda, K. Akiba, K.Suzuki and T. Takahashi, *Phys. Rev. Lett.*,**65**, 1271 (1990).
20. W. A. Little, *Phys. Rev.*, **134A**, 1416 (1964).
21. K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen, *Acta Cryst.*, **B37**, 1236 (1982).
22. F. Wudle, *J. Am. Chem. Soc.*, **103**, 7064 (1981).
23. G. Rindorf, H. Soling and N. Thorup, *Acta Cryst.*, **B38**, 2805 (1982).
24. K. Bechgaard, D. O. Cowan and A. N. Bloch, *J. C. S. Chem. Commun.*, 937 (1974); M. Williams, M. A. Beno, J. C. Sullivan, L. M. Banovetz, J. M. Braam, G. S. Blackman, C. D. Carlson, D. L. Greer and D. M. Loesing, *J. Am. Chem. Soc.*, **105**, 643 (1983).

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013

25. S. S. P. Parkin, Z. M. Engler, R. R. Schumaker, R. Lagier, V. Y.Lee, J. Vorion, K. Carneirs, J. C. Scott and R. L.Greene, *J. Phys. Colloq.*, **44**, C3-791 (1983); S. S. P. Parkin, Z. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Greene, *Phys. Rev. Lett.*, **50**, 270 (1983).
26. É. B. Yagubskii, I. F. Shchegolev, V. N. Laukihin, P. A. Kononovich, M. V. Karatsovnik, A. V. Zvarykina and L. I. Buravov. *JETP Lett.*, **39** (1), 12 (1984); V. F. Kaminskii, T. G. Prokhorova, R. P. Shibaeva and E. B. Yagubskii, *ibd*, **39** (1), 17 (1984).
27. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto and J. tanaka, *Chem. Lett.*, **1988**, 55 (1988); K. Oshima, H. Urayama, H. Yamochi and G. Saito, *Physca C*, **153–155**, 1148 (1988).
28. A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. Williams, W. K. Kwork, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, M. -H. Whangbo, *Inorg. Chem.*, **29**, 2555 (1990).
29. J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, M. -H. Whangbo, *Inorg. Chem.*, **29**, 3272 (1990).
30. A. F. Hebard, M. J. Rosseinski, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, **350**, 600 (1991).
31. M. J. Rosseinski, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haadon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak and A. V. Maskhija, *Phys. Rev. Lett.*, **66**, 2830 (1991).
32. S. P. Kelty, C. C. Chen and C. M. Lieber, *Nature*, **352**, 223 (1991).
33. A. Bondi, *J. Phys. Chem.* **68**, 441 (1964).
34. International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham (1968) p. 276.
35. V. M. Goldschmidt, *Trans. Farady Soc.*, **25**, 253 (1929).
36. I. D. Brown and R. D. Shannon, *Acta Cryst.*, **A29**, 266 (1973); I. D. Brown,*Structure and Bonding in Crystals*, Vol. 2, ed. M. O'Keeffe and A. Novrotsky, (Accademic Press, New York, 1981), Chap. 1, pp.1.
37. Z. D. Brown and D. Altermatt, *Act. Cryst.*, **B41**, 244 (1985).
38. D. Jérome and A. Mazavad, M. Ribault and K.Bechgaard, *J. Phys. (Paris) Lett.*, **41**, L95 (1980).
39. K. Bechgaard and D. Jérome, *Scientific American*, July, 50 (1982).
40. K. Bechgaard, K. Carneiro, M. Olsen, F. B. Rasmussen and C. S. Jacobsen, *Phys. Rev. Lett.*, **46**, 852 (1981).
41. B. Gallois, D. Chasseau, J. Gaultier, C. Hauw, A. Filhol and K. Bechgaard, *J. Phys. Colloq.*, **44**, C3-1071 (1983).
42. J. M. Williams, M. A. Beno, E. H. Appleman, J. M. Capriotti, F. Wudle, E. Aharon-Shalon and D. Nalewajek, *Mol. Cryst. Liq. Cryst.*, **79**, 319 (1982).
43. D. Mailly, M. Ribault and K. Bechgaard, *J. Phys. Colloq.*, **44**, C3-1037 (1983).
44. H. J. Schulz, *Physica*, **143B**, 456 (1986).
45. M. A. Beno, J. M. Williams, M. M. Lee and D. O. Cowan, *Solid State Commun.*, **44**, 1195 (1982).
46. M. R. Bryce and L. C. Murphy, *Nature*, **309**, 119 (1984).
47. J. M. Williams, M. A. Beno, J. C. Sullivan, L. M. Banovertz, J. M. Braam, G. S. Blackman, C. D. Carlson, D. L. Greer, D. M. Loesing and K. Carneiro, *J. Phys. Collq.*, **44**, C3-941 (1983).
48. D. Jérome, *J. Magn. and Magn. Mat.*, **31–34**, 20 (1983); J. M. Williams, M. A. Beno, J. C.Sullivan, L. M. Banovertz, J. M. Braam, G. S. Blackman, C. D. Carlson, D. L. Greene and D. M. Loessing, *Phys. Rev.*, **B28**, 2873 (1983).
49. K. Bechgaard, K. Carneiro, F. B. Rasmussen, G. Rindorf, G. Jacobsen, H. J. Pedersen and J. G. Scott, *J. Am. Chem. Soc.*, **103**, 2440 (1981); J. P. Pouget, G. Shirane, K.Bechgaard, J. M. Fabre, *Phys. Rev.* **B27**, 5203 (1983).
50. V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko, I. F. Shchegolev and E. B. Yagubskii, *JETP Lett.*, **41**, 81 (1985); K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura and T. Ishiguro, *J. Phys. Soc. Jpn.*, **54**, 1236 (1985); J. E. Schirber, L. J. Azevedo, J. F. Kwak, E. L. Venturini, P. C. W. Leung, M. A. Beno, H. H. Wang and J. M. Williams, *Phys. Rev.* **B33**, 1987 (1986).
51. J. M. Williams, *Synth. Met.* **23**, 3839 (1984).
52. H. H. Wang, *Inorg. Chem.*, **24**, 2465 (1985).
53. H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama and H. Inokuchi, *Chem. Lett.*, 463 (1988).
54. A. J. Schultz, H. H. Wang and J. M. Williams, *J. Am. Chem. Soc.*, **108**, 7853 (1986).
55. J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W. K. Kwok, M.-H. Whangbo and J. E. Schirber, *Science*, **252**, 1501 (1991).
56. K. D. Carlson, G. W. Crabtree, L. N. Hall, F. Behroozi, P. T. Copps, L. M. Sowa, L. Nunez M. A. Firestone, H. H. Wang, M. A. Beno, T. J. Emge and J. M. Williams, *Mol. Cryst. Liq. Cryst.*, **125**, 159 (1985); J. M. Williams, H. H. Wang, M. A. Beno, T. J. Emge, L. M. Sowa, P. T. Copps, F. Behroozi, L. N. Hall, K. D. Carlson and G. W. Crabtree, *Inorg. Chem.*, **23**, 3839 (1984).

57. T. J. Emge, P. C. W. Leung, M. A. Beno, H. H. Wang, M. A. Firestone, K. S. Webb, K. D. Carlson and J. M.Williams, *Mol. Cryst. Liq. Cryst.*, **132**, 363 (1986).
58. A. J. Schultz, M. A. Beno, U. Geiser, H. H. Wang, A. M. Kini and J. .M. Williams, *J. Solid State Chem.*, **94**, 352 (1991).
59. H. Mori (formerly H. Urayama), Superconductivity Research Laboratory, Nagoya, Japan, private communication.
60. G. Saito, *Mol. Cryst. Liq. Cryst.*, **181**, 65 (1990).
61. Y. Watanabe, H. Sato, T. Sasaki and N. Toyota, *J. Phys. Soc. Jpn.*, **60**, 3608 (1991).
62. W. E. Pickett, *Nature*, **351**, 602 (1991); A. W. Sleight, *Nature*, **350**, 557 (1991).
63. K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, K. Kubo and S. Kuroshima, *Nature*, **352**, 222 (1991).
64. P. W. Stephens, L. Mikaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich and K. Holezer, *Nature*, **351**, 632 (1991).
65. W. I. F. David, R. M. Ibberson, I. J. S. Dennis, J. P. Hare and K. Prassides, *Europhys. Lett.*, **18**, 219 (1992).
66. R. M. Fleming, A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, R. C. Haddon, S. M. Zahurak and A. V. Makhija, *Nature*, **352**, 787 (1991).
67. N. Metropolis and J. R. Reitz, *J. Chem. Phys.*, **19** (5), 555 (1951); R. Letter,*Phys. Rev.*, **99** (2), 510 (1951).
68. N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt and D. MacNair, *Phys. Rev. Lett.*, **14**, 225 (1965).
69. Z. Iqbal, R. H. Baughman, B. L. Ramakrishna, S. Khare, N. S. Murthy, H. J. Bornemann and D. E. Morris, *Science*, **254**, 826 (1991).
70. R. Foster, *Organic Charge-Transfer Complexes*, (Academic Press, London, 1970), Chap. 1, pp. 2.
71. R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950), **74**, 811 (1952); R. S. Mulliken, *J. Phys. Chem.*, Ithaca, **56**, 801 (1952).
72. H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949); N. S. Bayliss, *Quart. Rev.*, (London) **6**, 319 (1952).
73. The resonance leading to "charge-transfer forces" in Mulliken's model is equivalent to the delocalization of π-electrons in the free-electron model.
74. K. Shuler, *J. Chem. Phys.*, **20**, 1865 (1952).
75. J. C. A. Boeyens, *J. Phys. Chem.*, Ithaca, **71**, 2969 (1967).
76. S. Nagakura, *Quantum Theory of Chemical Bonding* (in Japanese), ed. T. Nakajima, H. Hosoya and S. Yonezawa, Iwanami, Tokyo, 1981, pp. 221.
77. J. M. Williams, H. H. Wang, J. J. Emage, U. Geiser, M. A. Beno, K. D. Carlson, R. J. Thorn, A. J. Schultz, M.-H. Whangbo, *Prog. Inorg. Chem.*, **35**, 51 (1987).
78. J. E. Schirber, E. L. Venturini, A. M. Kini, H. H. Wang, J. R. Whitworth and J. M. William, *Physica C*, **152**, 157 (1988); W. Kang, D. Jérome, C. Lenoir and P. Batail, *J. Phys. Condens, Matt.*, **2**, 1665 (1990).
79. G. Sparn, J. D. Thompson, S.-M. Huang, R. B. Kaner, F. Diederich, R. L. Whetten, G. Grüner and K. Holezer, *Science* **252**, 1829 (1991); Y. E. Schirber, D. L. Overmyer, H. H. Wang, J. M. Williams, K. D. Carlson, A. M. Kini, U. Welp and W. -K. Kwork, *Physica C*, **178**, 137 (1991).
80. N. H. Flecher, *The Chemical Physics of Ice* (Cambridge Univ. Press, London, 1970), Chap. 3, pp. 71.

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:21 18 February 2013