Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Characterization of a Structural Phase Transition in δ-$(ET)_2AuBr_2$ at 420K by ESR and Crystal Packing Studies

L. K. Montgomery [a], H. H. Wang [a], J. A. Schlueter [a], U. Geiser [a], K. D. Carlson [a], J. M. Williams [a], R. L. Rubinstein [a], T. D. Brennan [a], D. L. Stupka [a], J. R. Whitworth [a], D. Jung [b] & M.-H. Whangbo [b]
[a] Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL, 60439
[b] Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204
Version of record first published: 22 Sep 2006.

To cite this article: L. K. Montgomery , H. H. Wang , J. A. Schlueter , U. Geiser , K. D. Carlson , J. M. Williams , R. L. Rubinstein , T. D. Brennan , D. L. Stupka , J. R. Whitworth , D. Jung & M.-H. Whangbo (1990): Characterization of a Structural Phase Transition in δ-$(ET)_2AuBr_2$ at 420K by ESR and Crystal Packing Studies, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 197-208

To link to this article: http://dx.doi.org/10.1080/00268949008036004

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 197–208
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CHARACTERIZATION OF A STRUCTURAL PHASE TRANSITION IN δ-$(ET)_2AuBr_2$ AT 420K BY ESR AND CRYSTAL PACKING STUDIES

L. K. MONTGOMERY*, H. H. WANG, J. A. SCHLUETER, U. GEISER, K. D. CARLSON, J. M. WILLIAMS*, R. L. RUBINSTEIN, T. D. BRENNAN, D. L. STUPKA, and J. R. WHITWORTH
Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439

and

D. JUNG and M.-H. WHANGBO*
Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

Abstract The ESR lineshapes of δ- and α'-$(ET)_2AuBr_2$ (ET denotes bis(ethylenedithio)tetrathiafulvalene) were examined over a wide temperature range. The lineshape studies indicated that α'-$(ET)_2AuBr_2$ was stable from 300 to 460 K, where decomposition occurred. In contrast, δ-$(ET)_2AuBr_2$ was converted to α'-$(ET)_2AuBr_2$ in a few minutes at 420 K. Due to the heavily twinned nature of the crystals obtained, the α' product could not be unamiguously identified by X-ray crystallography and was characterized by ESR spectroscopy. The ESR lineshape behavior (100 to 300 K) of the thermally-derived α' modification was identical within experimental error to that of independently synthesized α'-$(ET)_2AuBr_2$. Crystal packing analysis showed that α'-$(ET)_2AuBr_2$ has more short C-H•••anion contacts per donor molecule than does δ-$(ET)_2AuBr_2$, thereby suggesting that α'-$(ET)_2AuBr_2$ is thermodynamically more stable than δ-$(ET)_2AuBr_2$.

INTRODUCTION

The salts of bis(ethylenedithio)tetrathiafulvalene have been the

* Authors to whom correspondence should be addressed.

focus of intense study[1] since ambient pressure superconductivity (T_c ~ 1.5 K) was first observed[2] and confirmed[3] in β-$(ET)_2I_3$ in 1984. Subsequently, nine additional salts of ET have exhibited superconductivity (T_c's ranging from 2.5 to 10.4 K) at ambient pressure: (β-$(ET)_2IBr_2$,[4] β-$(ET)_2AuI_2$,[5] α_t-$(ET)_2I_3$,[6,7] $(ET)_4Hg_{2.98}Br_8$,[8] ϵ_t-$(ET)_2I_3$,[9] γ-$(ET)_3(I_3)_{2.5}$,[10] θ-$(ET)_2$-$(I_3)_{1-x}(AuI_2)_x$(X<0.02),[11] κ-$(ET)_2(I_3)_{1-x}(AuI_2)_x$(X<0.006),[12] and κ-$(ET)_2Cu(NCS)_2$[13]). These account for over two-thirds of the known ambient pressure organic superconductors. Nonsuperconducting ET salts may become superconducting under pressure. For example, κ-$(ET)_4Hg_3Cl_8$ possesses T_c's of 1.8 and 5.3 K under pressures of 12 and 29 kbar, respectively.[14] β-$(ET)_2I_3$ is converted to an ordered high-T_c phase (T_c ~ 8 K), β^*-$(ET)_2I_3$, by the application of an anisotropic pressure of only 0.5 kbar.[15]

Recently, a number of novel, thermally-induced phase transformations of ET salts have been reported[6,7,9]; several yield superconductors. α-$(ET)_2I_3$(T_{MI} = 135 K), which is usually formed along with β-$(ET)_2I_3$ in the electrocrystallization route to $(ET)_2I_3$, is converted to α_t-$(ET)_2I_3$ upon heating at 70°C for several days.[6,7] The α_t-phase undergoes a superconducting transition near 8 K at ambient pressure. Although a structural study of α_t-$(ET)_2I_3$ is unavailable, the similarity of the T_c's of the α_t- and β^*- phases suggests that they are closely related in structure. ϵ-$(ET)_2I_3(I_8)_{0.5}$ is produced in the chemical oxidation of ET by iodine and is metallic down to 0.5 K.[9] This iodine-rich phase yields a superconducting material (T_c ~ 6-7 K) upon heating at reduced pressure. Both the α- and ϵ- phases possess a W-type interstacking packing mode,[1] implying that phase transformations may be facile in crystals containing the W-type packing motif. In keeping with this hypothesis, the conversion of α-$(ET)_2IBr_2$ (W-type) to β-$(ET)_2IBr_2$ at 416 K has been observed recently.[16]

In order to further explore the scope of thermal ET salt phase transformations, we have studied the ET/$AuBr_2^-$ system employing ESR spectroscopy and crystal packing studies. Three structural modifications have been reported for the electrocrystallization

products of ET in the presence of the $AuBr_2^-$ anion. The predominant species under slow crystal growth conditions (current density ~1μA/cm^2) is a semiconductor, α'-$(ET)_2AuBr_2$.[18] A second 2:1 salt, δ-$(ET)_2AuBr_2$, is also a semiconductor.[17] The third known phase is β''-$(ET)_2AuBr_2$[21]; it is metallic from ambient temperature to 1.4 K. In the following, we observe a novel thermal interconversion of the δ and α' modifications of $(ET)_2AuBr_2$ by ESR spectroscopy and discuss this transformation from the viewpoint of crystal packing.

EXPERIMENTAL

α'- and δ-$(ET)_2AuBr_2$ were both prepared by electrocrystallization of ET and NBu_4AuBr_2 in tetrahydrofuran at current densities of 1.0 and 5.5 μA/cm^2, respectively. The ESR experiments were carried out on an IBM ER200 X-band spectrometer equipped with an Oxford liquid helium cryostat and a VT4111 temperature controller for low and high temperature measurements. The unit cell parameters for the δ phase were determined by the precession film method: orthorhombic, **a** = 13.64 Å, **b** = 14.84 Å, **c** = 32.47 Å, V = 6,572 Å^3, in good agreement with reference 17, if the two-fold superstructure along the **a**-direction is taken into account.

RESULTS AND DISCUSSION

1. ESR Studies

In an attempt to observe a possible semiconducting to metallic phase transformation from α'- to β''-$(ET)_2AuBr_2$, a variable temperature ESR study was carried out on an α' crystal that was maintained in a fixed orientation. The small needle-like α' crystal possessed a room temperature ESR peak-to-peak linewidth of ~36 G. Since the temperature-dependent ESR linewidth behavior of α'-$(ET)_2AuBr_2$ had not been reported previously, the ESR signal of the crystal was carefully monitored from 300 to 100 K. The linewidth was approximately constant (36±2 G) down to 120 K; below this temperature it increased rapidly. The linewidth broadening below 120 K is most likely associated with a unit cell doubling, which has been observed crystallographically.[18] It is important to note that the linewidth behavior of the

semiconducting α' phase is completely different from that of the metallic β'' phase, whose linewidth decreases monotonically with decreasing temperature from ~44 G at 300 K to ~22 G at 100 K.[19] The α' crystal was then warmed from 100 to 300 K and slowly heated in the ESR cavity. ESR spectra were recorded at 20° intervals. Both the linewidth and relative spin susceptibility dropped slightly with increasing temperature. However, no unusual features were observed until the sample decomposed near 460 K. Evidently, the α' structure does not undergo high temperature structural or electronic phase transformations.

The ESR lineshape of δ-$(ET)_2AuBr_2$ was monitored next as a function of temperature. The δ-phase crystals (thin rectangular platelets) possessed unit cell parameters consistent with the published values.[17] The room temperature ESR linewidth of δ-$(ET)_2AuBr_2$ is near 10 G, which is much narrower than those of either the α' or the β'' phases. As shown in Figure 1, the ESR linewidth

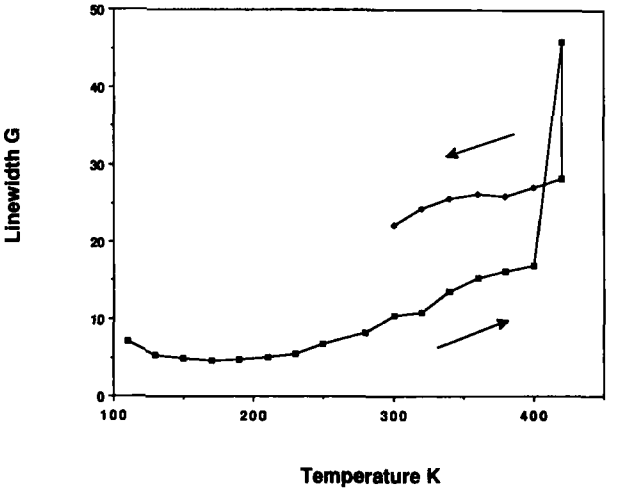


FIGURE 1 The ESR peak-to-peak linewidth (100-400 K) of δ-$(ET)_2AuBr_2$ (hollow points), and high temperature (300-420 K) ESR linewidth change of $\delta \rightarrow \alpha'$-$(ET)_2AuBr_2$ (solid points).

drops to ~5 G at 170 K and then rises slightly. The relative spin susceptibility, which is proportional to the integrated ESR intensity, decreases by an order of magnitude from 300 to 100 K. The low temperature ESR behavior of δ-$(ET)_2AuBr_2$ is consistent with its semiconducting properties. The δ-phase crystal was warmed from 100 to 300 K and then heated at 20 K increments (Figure 1). The linewidth and the spin susceptibility both increase with increasing temperature. The linewidth changes from 10 G at 300 K to 17 G at 400 K. At 420 K, a series of lineshape changes occur. The 17 G transition totally vanishes and is replaced by a distorted lineshape of ~45 G. The new absorption changes shape over the course of a few minutes and finally stabilizes into a well-defined ESR transition with a linewidth of 28 G at 420 K. The heat-treated δ-phase crystal was then cooled slowly to room temperature. A quantitative ESR lineshape analysis[20] of the spectrum at 400 K revealed that the heat converted product consisted of ~90% of a 31 G phase and 10% of a 19 G phase, presumably unreacted δ phase.

Attempts to obtain precise single crystal unit cell parameters of the heat-converted product were unsuccessful due to the heavily twinned nature of the crystals obtained. Nevertheless, the 6.76 Å c-axis of the α'-phase[18] was recognizable on Weissenberg photographs in spite of the considerable diffuseness of the diffraction pattern within the a*c*-plane. Twinning is expected because of the symmetry reduction from the orthothombic δ phase to the monoclinic α' structure. In order to confirm the δ to α' phase conversion, three δ-$(ET)_2AuBr_2$ crystals having ESR linewidths near 10 G were heated in an oven at 425 K for 30 min., resulting in product crystals that possessed room temperature linewidths of 33-35 G. Since the X-ray crystallographic identification of the α' product was not definitive, one of the heat converted crystals was characterized by its low temperature ESR linewidth behavior. The peak-to-peak linewidth and relative spin susceptibility are shown in Figure 2. The invariance of

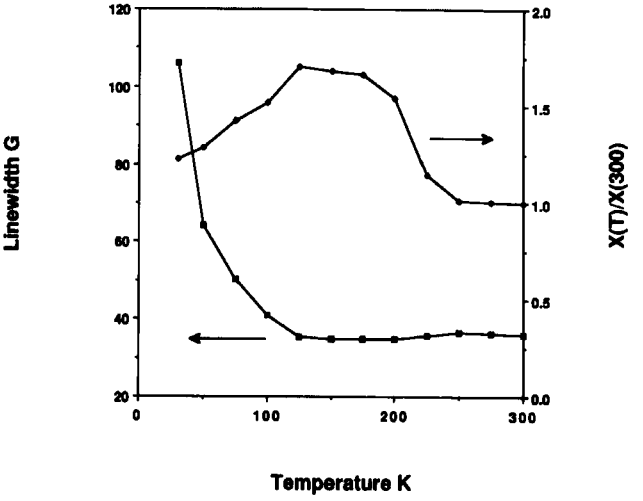
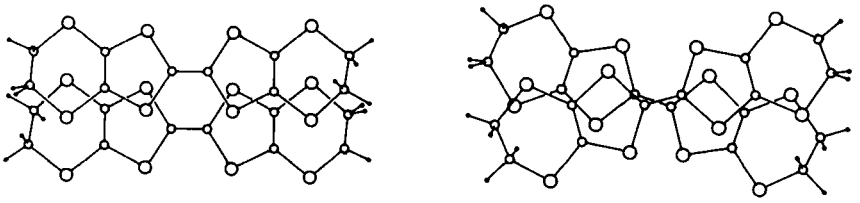


FIGURE 2 Temperature-dependent ESR peak-to-peak linewidth and relative spin susceptibility of the heat-converted α'-$(ET)_2AuBr_2$.

the linewidth (~37 G) above 125 K and a sharp rise below are highly characteristic of α'-$(ET)_2AuBr_2$. Temperature dependent ESR lineshape profiles of this type should prove valuable in the future for identifying the products of thermal phase transitions, because the resulting crystals are frequently microcrystalline or twinned, rendering X-ray crystallographic methods of identification difficult or impossible.

2. Donor Stacking in δ- and α'-$(ET)_2AuBr_2$

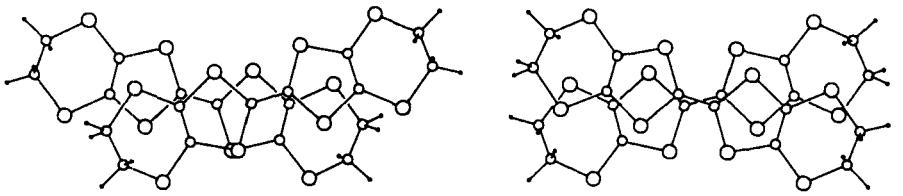
Characteristic features of a donor stack in organic donor salts may be described by the relative arrangement of adjacent donor molecules along the directions parallel and perpendicular to the central C=C bond of the donor molecule.[1] Along the central C=C bond, two adjacent donor molecules may have a bond-over-bond (BOB) or a bond-over-ring (BOR) arrangement. When two adjacent donor molecules slip along the direction perpendicular to the central C=C bonds, the resulting arrangement may be such that the central C=C bonds are either parallel (mode-b) or make an acute angle (mode-c). Figures 3a,b show



(a) (b)

FIGURE 3 Projection views of donor pairs in a stack of δ-$(ET)_2AuBr_2$: (a) the BOB/mode-b arrangement and (b) the BOB/mode-c arrangement.

projection views of two consecutive donor pairs in a donor stack of δ-$(ET)_2AuBr_2$: Both pairs have a BOB arrangement. One pair has a mode-b donor slipping as shown in Figure 3a (i.e., BOB/mode-b), and the other has a mode-c donor slipping as shown in Figure 3b (i.e., BOB/mode-c). Figures 4a,b show projection views of two consecutive donor pairs in a donor stack of α'-$(ET)_2AuBr_2$: Both pairs have a mode-c donor



(a) (b)

FIGURE 4 Projection views of donor pairs in a stack of α'-$(ET)_2AuBr_2$: (a) the BOR/mode-c arrangement and (b) the BOB/mode-c arrangement.

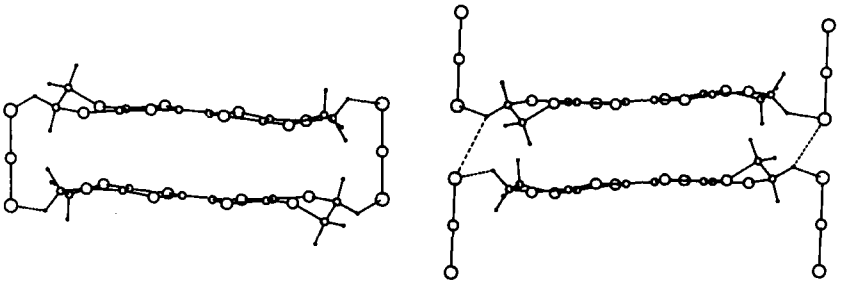
slipping. One pair has a BOR arrangement as shown in Figure 4a (i.e., BOR/mode-c), and the other pair has a BOB arrangement as shown in Figure 4b (i.e., BOB/mode-c). The crystal packing of β''-$(ET)_2AuBr_2$ is not related to that of either the δ- or the α'-phases.[21]

3. Phase Transition and C-H···Donor vs C-H···Anion Interactions

The δ - to α'-phase transition, described above, suggests that the α-phase is thermodynamically more stable than the δ-phase. We

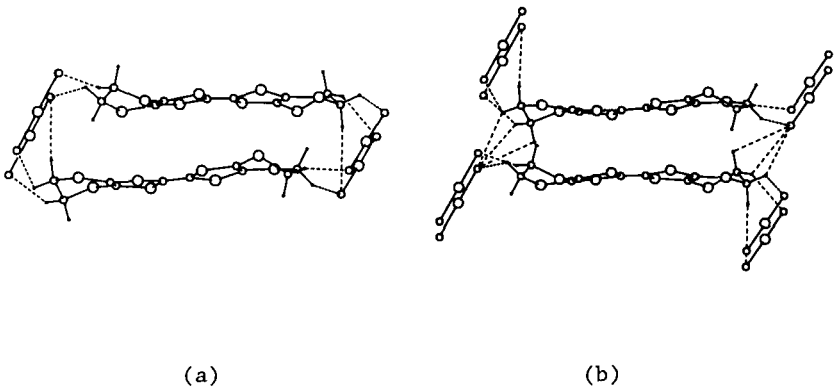
now examine a probable origin of this phase change. Over the past years it has been recognized that crystal packing patterns and, hence, physical properties of organic donor salts are critically influenced by weakly hydrogen-bonding C-H•••donor and C-H•••anion interactions.[22-24] Ab initio SCF-MO/MP2 calculations on H_3C-H•••X^- (X^- = I-I-I$^-$, Br-I-Br$^-$, Cl-I-Cl$^-$) and H_3C-H•••YH_2 (Y = O, S, Se) show that, at their optimum H•••X^- and H•••Y distances, the C-H•••anion interactions C-H•••I, C-H•••Br, and C-H•••Cl are slightly more attractive than the C-H•••donor interaction C-H•••O,[22] but are several times more attractive than the C-H•••donor interactions C-H•••S and C-H•••Se.[22] Therefore, for given 2:1 salts of ET, a phase with more C-H•••anion contacts per donor molecule is expected to be more stable than a phase with less C-H•••anion contacts per donor molecule. This prediction is consistent with the thermally-induced phase transition α- to α_t-$(ET)_2I_3$.[24a] In a number of physical properties, α_t-$(ET)_2I_3$ and β^*-$(ET)_2I_3$ are similar, and β^*-$(ET)_2I_3$ has more C-H•••I contacts per ET than does α-$(ET)_2I_3$.

As described in an earlier section, the donor stack of δ-$(ET)_2AuBr_2$ has the BOB/mode-b and BOB/mode-c arrangements (Figure 3); while the donor stack of α'-$(ET)_2AuBr_2$ has the BOR/mode-c and BOB/mode-c arrangements (Figure 4). Thus an essential structural change associated with the δ- to α'-phase transition is the stacking rearrangement from BOB/mode-b to BOR/mode-c. The short C-H•••Br contacts in δ-$(ET)_2AuBr_2$ and α'-$(ET)_2AuBr_2$ are shown in Figure 5 and 6, respectively, where the H•••Br contact distances less than the van



(a) (b)

FIGURE 5 Short C-H ••• anion contacts in δ-$(ET)_2AuBr_2$ associated with (a) the BOB/mode-b and (b) the BOB/mode-c arrangements.



(a) (b)

FIGURE 6 Short C-H ••• anion contacts in α'-$(ET)_2AuBr_2$ associated with (a) the BOR/mode-c and (b) the BOB/mode-c arrangements.

der Waals radii sum (3.35Å) are shown by dashed lines. These H•••Br distances are 2.74, 3.00, 3.09, 3.18, 3.30, and 3.34 Å in $\alpha'(ET)_2AuBr_2$, while they are 3.20, 3.23 and 3.27 Å in δ-$(ET)_2AuBr_2$. Therefore, the donor molecule has more short C-H•••anion contacts in α'-$(ET)_2AuBr_2$ than in δ-$(ET)_2AuBr_2$. Though not shown, the donor molecule has more short C-H•••donor contacts in δ-$(ET)_2AuBr_2$. A general point worth noting is that the δ- to α'-phase transformation is consistent with the prediction that, given a 2:1 ET salt, a phase with more C-H•••anion contacts is more stable than an alternative phase with less C-H•••anion contacts.

4. Concluding Remarks

ESR lineshape studies have demonstrated that δ-$(ET)_2AuBr_2$ is transformed into α'-$(ET)_2AuBr_2$ at 420 K. Crystal packing analysis of δ- and α'-$(ET)_2AuBr_2$ reveals that α'-$(ET)_2AuBr_2$ has more short C-H•••anion contacts per donor molecule than does δ-$(ET)_2AuBr_2$. The essential structural change associated with the δ- to α'-phase transformation is the change in stacking rearrangement from BOB/mode-b to BOR/mode-c. The BOR arrangement of adjacent donor molecules in a stack appears to be important in providing short C-H•••anion contacts and stabilization of the crystal lattice. In general, donor salts of

ET containing only the BOB arrangement between adjacent donor molecules are expected to be susceptible to thermally-induced phase transitions. Temperature dependent lineshape comparisons as described in the present work should prove to be a convenient and valuable tool for studying such phase changes.

ACKNOWLEDGMENTS

Work at Argonne National Laboratory and at North Carolina State University is sponsored by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38 and Grant DE-FG05-86ER45259, respectively. L.K.M. is a Scientist in Residence, sponsored by the Argonne Division of Educational Programs, on leave from the Department of Chemistry, Indiana University, Bloomington, IN; J.A.S., R.L.R., T.D.B., D.L.S., and J.R.W. are undergraduate student research participants sponsored by the Argonne Division of Educational Programs from Valparaiso University (Valparaiso, IN), Carnegie-Mellon University (Pittsburgh, PA), University of Notre Dame (Notre Dame, IN), Illinois Benedictine College (Lisle, IL), and Transylvania University (Lexington, KY), respectively.

REFERENCES

1. J.M. Williams, H.H. Wang, T.J. Emge, U. Geiser, M.A. Beno, P.C.W. Leung, K.D. Carlson, R.J. Thorn, A.J. Schultz, M.-H. Whangbo, Prog. Inorg. Chem., 35, 51 (1987).
2. E.B. Yagubskii, I.F. Shchegolev, V.N. Laukhin, P.A. Kononovich, M.W. Karatsovnik, A.V. Zvarykina, L.I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz., 39, 12 (1984); JETP Lett. (Engl. Transl.), 39, 12 (1984).
3. J.M. Williams, T.J. Emge; H.H. Wang, M.A. Beno, P.T. Copps, L.N. Hall, K.D. Carlson, G.W. Crabtree, Inorg. Chem., 23, 2558 (1984).
4. 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, G.W. Crabtree, Inorg. Chem., 23, 3839 (1984).
5. H.H. Wang, M.A. Beno, U. Geiser, M.A. Firestone, K.S. Webb, L. Nuñez, G.W. Crabtree, K.D. Carlson, J.M. Williams, L.J. Azevedo, J.F. Kwak, J.E. Schirber, Inorg. Chem., 24, 2465 (1985).
6. G.O. Baram, L.I. Buravov, L.S. Degtyarev, M.E. Kozlov, V.N. Laukhin, E.E. Laukhina, V.G. Onishchenko, K.I. Pokhodnya, M.K. Sheinkman, R.P. Shibaeva, E.B. Yagubskii, JETP Lett. (Engl. Transl.), 44, 376 (1986).
7. D. Schweitzer, P. Bele, H. Brunner, E. Gogu, U. Haeberlen, I.

Hennig, I. Klutz, R. Swietlik, H.J. Keller, Z. Phys., B67, 489 (1987).
8. R.N. Lyubovskaya, E.I. Zhilyaeva, S.I. Pesotskii, R.B. Lyubovskii, L.O. Atovmyan, O.A. D'yachaenko, T.G. Takhirov, JETP Lett. (Engl. Transl.), 46, 188 (1987).
9. V.A. Merzhanov, E.E. Kostyuchenko, V.N. Laukhin, R.M. Lobkovskaya, M.K. Makova, R.P. Shibaeva, I.F. Shchegolev, E.B. Yagubskii, JETP Lett. (Engl. Transl.), 41, 179 (1985).
10. R.P. Shibaeva, V.F. Kaminskii, E.B. Yagubskii, Mol. Cryst. Liq. Cryst., 119, 361 (1985).
11. Y. Kobayashi, R. Kato, A. Kobayashi, Y. Nishio, K. Kajita, W. Sasaki, Chem. Lett., 789, 833 (1986).
12. A. Kobashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, Chem. Lett., 459 (1987).
13. H. Urayama, H. Yamochi, G. Saito, K. Nozama, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, J. Tanaka, Chem. Lett., 55 (1988).
14. (a) R.N. Lyubovskaya, R.B. Lyubovskii, R.P. Shibaeva, M.Z. Aldoshina, L.M. Goldenberg, L.P. Rozenberg, M.L. Khidekel, Yu. F. Shulpyakov, JETP Lett., 42, 468 (1987).
(b) R.B. Lyubovskii, R.N. Lyubovskaya, N.V. Kapustin, Sov. Phys. JETP, 66, 1063.
15. (a) V.N. Laukhin, E.E. Kostyuchenko, Yu. V. Sushko, I.F. Shchegolev, E.B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz., 41, 68 (1985).
(b) K. Murata, M. Tokumoto, H. Aanzai H. Bando, G. Saito, K. Kajimura, T. Ishiguro, J. Phys. Soc. Jpn., 54, 1236 (1985).
(c) H. Veith, C.P. Heidmann, F. Gross, A. Lerf, K. Andres, D. Schweitzer, Solid State Commun., 56, 1015 (1985).
(d) J.E. Schirber, J.F. Kwok, M.A. Beno, H.H. Wang, J.M. Williams, Physica, 143B, 343 (1986).
16. H.H. Wang, K.D. Carlson, L.K. Montgomery, J.A. Schlueter, C.S. Cariss, W.K. Kwok, U. Geiser, G.W. Crabtree, J.M. Williams, Solid State Commun., 66, 1113 (1988).
17. T. Mori, F. Sakai, G. Saito, H. Inokuchi, Chem. Lett., 1589 (1986).
18. M.A. Beno, M.A. Firestone, P.C.W. Leung, L.M. Sowa, H.H. Wang, J.M. Williams, M.-H. Whangbo, Solid State Commun., 57, 735 (1986).
19. (a) I.D. Parker, S.D. Obertelli, R.H. Friend, D.R. Talham, M. Kurmoo, P. Day, J.A.K. Howard, A. Stringer, Synth. Met., 19, 185 (1987).
(B) M. Kurmoo, D.R. Talham, P. Day, I.D. Parker, R.H. Friend, A.M. Stringer, J.A.K. Howard, Solid State Commun., 61, 459 (1987).
20. L.K. Montgomery, U. Geiser, H.H. Wang, M.A. Beno, A.J. Schultz, A.M. Kini, K.D. Carlson, J.M. Williams, J.R. Whitworth, B.D. Gates, C.S. Cariss, C.M. Pipan, K.M. Donega, C. Wenz, W.K. Kwok, G.W. Crabtree, Synth. Met., 27, A195 (1988).
21. T. Mori, F. Sakai, G. Saito, H. Inokuchi, Chem. Lett., 1037 (1986).
22. M.-H. Whangbo, D. Jung, M. Evain, J.J. Novoa, F. Mota, S. Alvarez, J.M. Williams, M.A. Beno, A.M. Kini, H.H. Wang, J.R.

Ferraro, The Physics and Chemistry of Organic Superconductors, G. Saito, S. Kagoshima, Eds.: Springer-Verlag, in press.

23. (a) M.-H. Whangbo, J.M. Williams, A.J. Schultz, T.J. Emge, M.A. Beno, J. Am. Chem. Soc., 109, 90, (1987).
(b) M.-H. Whangbo, J.M. Williams, A.J. Schultz, M.A. Beno, Organic and Inorganic Low-Dimensional Crystalline Materials, P. Delhaes, M. Drillon, Eds.: Plenum, New York, 1987, P 333.

24. (a) H.H. Wang, J.R. Ferraro, K.D. Carlson, L.K. Montgomery, U. Geiser, J.R. Whitworth, J.A. Schlueter, J.M. Williams, S. Hill, M.-H. Whangbo, M. Evain, J.J. Novoa, Inorg. Chem., 28, 2267 (1989).
(b) J.R. Ferraro, H.H. Wang, U. Geiser, A.M. Kini, M.A. Beno, J.M. Williams, S. Hill, M.-H. Whangbo, M. Evain, Solid State Commun., 68, 917 (1988).
(c) A.M. Kini, M.A. Beno, D. Son, H.H. Wang, K.D. Carlson, L.C. Porter, U. Welp, B.A. Vogt, J.M. Williams, D. Jung. M. Evaom, M.-H. Whangbo, D.L. Overmyer, J.E. Schirber, Solid State Commun., 69, 501 (1989).
(d) D. Jung, M. Evain, J.J. Novoa, M.-H. Whangbo, M.A. Beno, A.M. Kini, A.J. Schultz, J.M. Williams, P.J. Nigrey, Inorg. Chem., in press.