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

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Version of record first published: 24 Sep 2006.

To cite this article: Lawrence K. Montgomery , Timothy Burgin , Thomas Miebach , Dennis Dunham , John C. Huffman & James E. Schirber (1996): Characterization of the Electrocrystallization Products of Bis(ethylenedithio)tetraselenafulvalene (BETS) and Tetrabutylammonium Tetrachlorogallate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 73-84

To link to this article: http://dx.doi.org/10.1080/10587259608037912

Mol. Cryst. Liq. Cryst., 1996, Vol. 284, pp. 73–84
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CHARACTERIZATION OF THE ELECTROCRYSTALLIZATION PRODUCTS OF BIS(ETHYLENEDITHIO)TETRASELENAFULVALENE (BETS) AND TETRABUTYLAMMONIUM TETRACHLOROGALLATE

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Abstract Nine different crystal morphologies have been isolated from the electrocrystallization products of bis(ethylenedithio)tetraselenafulvalene (BETS) and tetrabutylammonium tetrachlorogallate. The morphologies have been examined by X-ray crystallography and electrical transport measurements and have been assigned to several different crystal systems: κ-, λ-, and κ'-$(BETS)_2GaCl_4$, α-$(BETS)_3GaCl_4$•TCE, and an incompletely characterized semiconductor. In experiments designed to gain some understanding of the variable resistive superconducting transition temperatures (T_c) in λ-$(BETS)_2GaCl_4$, the influence of gold paste on the AC susceptibility T_c was examined: gold paste raises the onset of superconductivity, and the effect is reversible. In related studies, it was found that isotropic pressure lowers T_c in λ-$(BETS)_2GaCl_4$ by -0.31 K/kbar. These observations are discussed.

INTRODUCTION

In preliminary studies of the electrocrystallization products of BETS and tetrabutylammonium tetrachlorogallate, a 2:1 kappa-phase salt, κ-$(BETS)_2GaCl_4$, was identified as the major product under the reaction conditions employed (1,1,2-trichloroethane (1,1,2-TCE): 5% ethanol by volume, current density 0.1-1 $\mu A/cm^2$, 40°C).[1,2] The resistivity-temperature profile of this material was interesting: the resistivity decreased from room temperature (8(6) x 10^{-2} Ωcm) to 265 K, increased, went through a maximum, and then decreased sharply. It was not possible at the time, however, to obtain a reproducible profile below 80 K.

A second minor phase consisting of exceedingly small black needles no larger than a few tenth of a μg was noted in the first κ-$(BETS)_2GaCl_4$ preparations. Subsequent characterization of the needles indicated that they were a superconductor, λ-$(BETS)_2GaCl_4$, with a resistive transition 5.5 K higher than any previously known organic superconductor containing selenium (T_c = 7.5 K, onset).[3,4] Interestingly, some

samples of λ-$(BETS)_2GaCl_4$ possessed resistive onsets as high as 10 K.[3,4] In such cases, the width of the transition also increased, but the position of zero resistance remained the same. Differences in cooling rates did not seem to be responsible for the difference in resistive onsets. No correlation between cooling rate and T_c was seen in samples cooled to 4 K over periods varying from 4-14 h. Since the crystals used in the λ-$(BETS)_2GaCl_4$ investigation were very small, the gold paste employed to affix the gold leads in the four-probe resistance measurements covered a significant portion of the crystal surface. One plausible origin of the spectrum of transitions is pressure/stress effects resulting from the application of the gold paste.

The present study was initiated to explore this hypothesis. Complementary AC susceptibility measurements (modulation field 60 A/m, 100 Hz) confirmed superconductivity in λ-$(BETS)_2GaCl_4$ (midpoint 4.5 K, ΔT = 1 K).[4] Figure 1 shows the in-phase (χ') and imaginary (χ'') components of the susceptibility from 2.3 K to 20 K. The signal to noise ratio in χ' in Figure 1 (80 well-formed λ-$(BETS)_2GaCl_4$ crystals) is 285:1. There is no evidence of crystals with abnormally high T_c's in Figure 1 (inset). In resistive samples, roughly one-half of the crystals exhibit broad transitions with elevated T_c's. As a first step in exploring these contrasting results, the effect of gold paste on the AC susceptibility of λ-$(BETS)_2GaCl_4$ was examined.

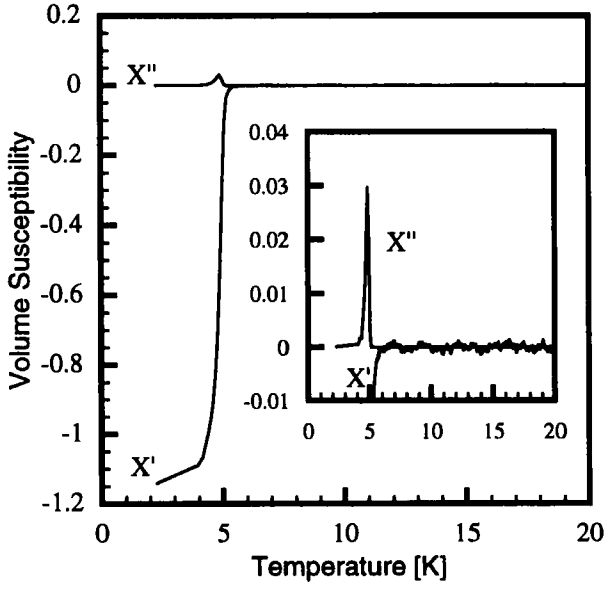

FIGURE 1 Volume susceptibility *vs.* temperature for λ-$(BETS)_2GaCl_4$. The inset shows an expanded view of the χ' and χ'' components near the superconducting transition.

EXPERIMENTAL

Materials

BETS[5] and tetrabutylammonium tetrachlorogallate[6] were prepared following published procedures.[7] 1,1,2-TCE and 1,1,1-TCE were distilled from P_2O_5 under nitrogen and passed through Woelm neutral alumina (activity one) immediately prior to use. Commercial absolute ethanol was used as received.

Electrocrystallization Procedures

The electrocrystallization procedures have been described previously.[8] The electrochemical cells were maintained under a positive pressure of nitrogen in thermostated (±0.1°C), vibrationally-isolated cell boxes. All electrocrystallizations were conducted in the constant current mode. The effects of solvent composition, temperature, and current density were systematically explored.

AC Susceptibility and AC and DC Resistance Measurements

AC susceptibility and AC and DC resistance measurements were carried out employing a Lake Shore Cryotronics, Inc., 7110 series susceptometer system equipped with the model 700R2 AC/DC resistance option.

For the AC and DC resistance measurements, a four-probe procedure was utilized.[9] Gold wires (99.9%, 7 x 10^{-4} in od, 1-3% elongation) were attached to suitable crystals with conductive gold paste (Pelco SEM-Au gold liquid, Ted Pella, Inc.). The crystal mounts were cooled to 4 K over 2-14 h periods, and resistivity data were collected on warming to room temperature.

AC susceptibility measurements were made with a modulation field and frequency of 60 A/m and 100 Hz, respectively. Numerous small, black, shiny needles with rhomboidal ends (~0.80 mg) were placed in a Delrin sample holder and cooled from room temperature to 4 K. Further cooling to 2.3 K was achieved by pumping on the helium cryostat, but temperature control was more difficult below 4 K. AC susceptibilities were recorded at temperature intervals of 0.1 K from 2.3 K to 20 K. Both the in-phase or real (χ') and imaginary (χ'') components were measured as volume susceptibilities (dimensionless SI units).

X-ray Crystallography

The general experimental and analysis procedures have been described previously.[10] A suitable crystal was affixed to the end of a glass fiber using silicone grease (low temperature) or Duco cement and transferred to a Picker four-cycle goniostat equipped with a Furnas monochromator (HOG crystal) and a picker X-ray generator (Mo Kα

radiation, $\lambda = 0.71069$Å). Data were collected using a continuous $\theta/2\theta$ scan technique with fixed backgrounds at each extreme of the scan, and three standard reflections were collected every 300 reflections.

TABLE 1 Summary of experimental data for X-ray crystallography.

	Kappa	Kappa	Alpha
Formula	$C_{20}H_{16}Cl_4GaSe_8S_8$	$C_{20}H_{16}Cl_4GaSe_8S_8$	$C_{32}H_{27}Cl_7GaSe_{12}S_{12}$
F. W.	1356.04	1356.04	2061.70
Cryst. Dimens. (mm)	0.05 × 0.20 × 0.21	0.01 × 0.10 × 1.25	0.07 × 0.07 × 0.65
ρ(calcd.) (g cm^{-3})	2.609	1.252	2.492
Temp. (K)	105	293	104
Abs. Coeff. (cm^{-1})	99.453	47.741	91.852
Absorption, max.:	0.229	0.921	0.390
min.:	0.610	0.612	0.468
F(000), e	635	635	969
Min. *hkl*	0, 0, 0	0, 0, -9	0, 0, 0
Max. *hkl*	12, 37, 8	40, 11, 8	13, 39, 12
Scan Speed (°/min)	4.0	8.0	8.0
2θ Range (°)	4 - 45	6 - 45	6 - 45
Total Data Collected	2659	5014	5149
Unique Data	2298	2343	3650
Observed Data ($\|F\| > 2.33\ \sigma(F)$)	1358	1422	1853
No. of Parms Refined	139	191	282
Final Shift/Error	0.02	0.21	0.12
Max. Resid. Density (e/Å^3)	2.37	0.91	1.35
R(F)	0.084	0.066	0.060
$R_w(F)$	0.080	0.052	0.057
GOF = $(\Sigma w(\|F_o\|-\|F_c\|)^2/(No-Nv))^{1/2}$	2.286	1.107	1.998

After correction for Lorentz, polarization and absorption terms (analytical), the structure was solved using direct methods (MULTAN 78) and Fourier techniques and refined by a full-matrix least squares procedure. Hydrogen atoms were placed in fixed,

idealized positions for the last cycles of refinement, and the carbon atoms refined isotropically. Table 1 summarizes the experimental parameters for the data collection for three different phases.

Pressure-RF Impedance Studies

An rf impedance technique described previously[11] was used to explore the effect of isotropic pressure on the T_c of λ-$(BETS)_2GaCl_4$. Pressures up to 5 kbar were generated by careful isobaric freezing of ^4He around the sample.[12]

RESULTS AND DISCUSSION

Crystal Growth

Prior to performing the AC susceptibility-gold paste experiment, a systematic survey of crystal growth conditions was carried out to optimize the quantity and quality of λ-$(BETS)_2GaCl_4$ crystals. Although a number of different solvents were examined initially, most of the study utilized mixtures of 1,1,2-TCE, 1,1,1-TCE, and absolute ethanol. 1,1,1-TCE was first employed as a solvent when it was purchased by accident.[13] It was found that the substitution of the 1,1,1-isomer for the 1,1,2-isomer markedly favored the formation of λ-$(BETS)_2GaCl_4$ over κ-$(BETS)_2GaCl_4$. Solvent composition, temperature (30-50°C), and current density were systematically explored. The best quality crystals (1000 x 100 x 50 μm) were obtained from a 90:10 mixture of 1,1,1-TCE: 1,1,2-TCE with 5% ethanol by volume (CD = 0.3 $\mu A/cm^2$, 50°C). Although it remains unclear why, the electrocrystallization properties of 1,1,1-TCE and 1,1,2-TCE are significantly different. Mixtures of these two solvents have proven useful in other applications.

Several different crystal morphologies were noted in the optimization experiments. The characterization of these materials is discussed below.

Gold Paste-AC Susceptibility Study

The volume susceptibility of a large number of carefully-selected, rhomboidal needles characteristic of the λ-phase of $(BETS)_2GaCl_4$ was measured as a function of temperature before and after the application of the same gold paste that was used in the resistivity experiments.

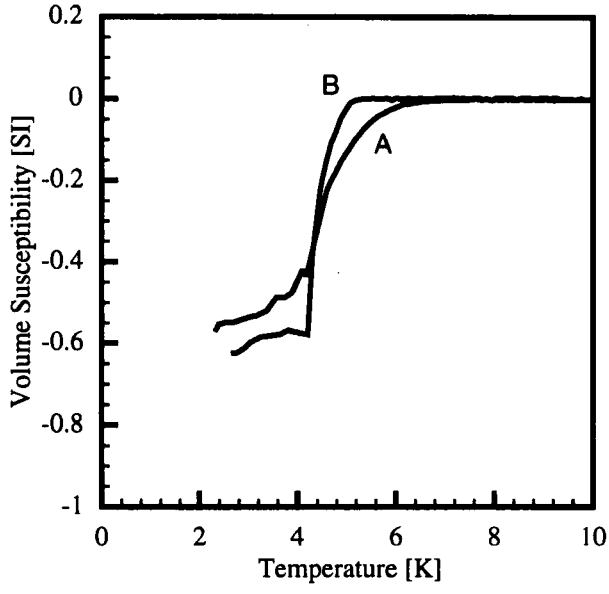

FIGURE 2 Volume susceptibility *vs.* temperature for λ-$(BETS)_2GaCl_4$. Plot A is for crystals with gold paste applied. Plot B is for the sample after removal of the gold paste.

The starting sample exhibited a typical sharp transition with a diamagnetic onset in χ' at slightly over 5 K. The crystals were thoroughly coated with gold paste, and the paste was permitted to dry for ~24 h. When the sample was rerun, the onset of superconductivity increased to almost 7 K (Figure 2). Most interestingly, however, the process was reversible. The gold paste was removed with 2-butoxyethyl acetate. The sample was dried and reweighed. Visual inspection of the crystals showed no sign of surface degradation, but they were fractured into smaller pieces. When the susceptibility was rerun, the onset returned to 5 K (Figure 2). Considering experimental errors and possible changes in demagnetization when the crystals broke into smaller pieces, the initial and final values of the volume susceptibility at 3 K are in reasonable agreement. The experiment is reproducible.

Pressure-T_c Study

The gold paste-T_c results could reasonably be associated with pressure effects related to differences in the coefficients of expansion of the gold paste and the λ-$(BETS)_2GaCl_4$ crystals. In order to evaluate this possibility, the effect of isotropic pressure on T_c was studied. An rf impedance technique was used to measure T_c. Results up to 5 kbar pressure are shown in Figure 3.

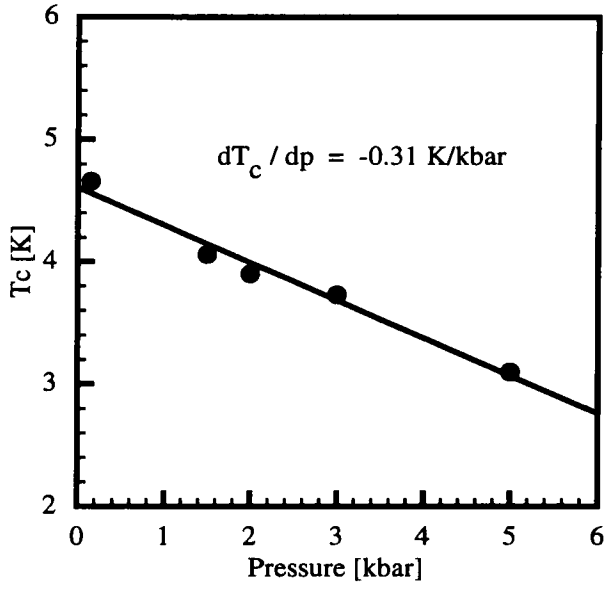

FIGURE 3 The effect of isotropic pressure on T_c in λ-$(BETS)_2GaCl_4$.

The derivative of T_c with respect to pressure is slightly negative (dT_c/dP = -0.31 K/kbar). A negative derivative is typical for organic superconductors, but the value for λ-$(BETS)_2GaCl_4$ is relatively small. From the magnitude of the derivative, it is doubtful that the paste is raising the T_c through isotropic pressure; 6 kbar of negative pressure would be required. Apiezon grease exerts a positive pressure of 0.3 kbar in this temperature range.[14] Anisotropic effects on pressure cannot be ruled out by these experiments.

Characterization of the Various Crystallographic Phases Obtained from the BETS-Tetrachlorogallate Electrocrystallization Studies

One plausible mechanism for the elevation of the T_c of λ-$(BETS)_2GaCl_4$ by the application of gold paste is the formation of a new phase with a higher T_c. Perhaps the paste induces some subtle ordering of molecular structure that raises T_c through anisotropic pressure. A single crystal X-ray study of λ-$(BETS)_2GaCl_4$ was carried out at 111 K to extend our previous structural studies at 293 K (Tables 1 and 2).[4]

TABLE 2 Summary of crystallographic data for various crystals of BETS with $GaCl_4^-$.

Phase	Kappa	Kappa	Lambda	Lambda	Kappa'	Alpha
Temperature	105 K	293 K	111 K	293 K	293 K	104 K
Space Group	Pnma	Pnma	$P\bar{1}$	$P\bar{1}$	C2/c	Pnma
a(Å)	11.537	11.675	15.905	16.165	37.803	12.756
b(Å)	35.739	35.940	18.435	18.612	11.203	38.204
c(Å)	8.373	8.471	6.535	6.608	8.522	11.274
α(deg)	90	90	98.64	98.41	90	90
β(deg)	90	90	95.96	96.69	94.83	90
γ(deg)	90	90	112.21	112.56	90	90
V(Å^3)	3452	3555	1727	1783	3596	5494
Z	4	4	2	2	4	4

No major structural changes were observed in the λ-phase between 293 K and 111 K. Moreover, there was no obvious structural disorder at 111 K. The 111 K structure may be irrelevant to the disorder argument, however, since there is a dramatic change from semiconductive to metallic behavior in the resistivity λ-$(BETS)_2GaCl_4$ at 95 K.[4] A 20 K structure is in progress to see if the well-ordered, triclinic $P\bar{1}$ structure is maintained down to the region where superconductivity is observed.

Nine different crystal morphologies were identified in the electrocrystallization studies outlined above. Eight are shown in Figure 4. Only one small needle of the ninth form was observed. Its molecular composition was $(BETS)_3GaCl_4$ • 1,1,2-TCE. The crystal packing was the α structural motif. The single crystal was lost during the X-ray experiment.

Crystals grown at 0.5 μA/cm^2 in 1,1,2-TCE:5% ethanol usually occurred as black rhombic prisms (morphologies **1** and **2**). Occasionally, well-formed crystals of several other geometries were observed. Their morphologies were: black acicular prisms with rhombic (**6**) or orthorhombic (**7**) ends, planar truncated pyramids (**3**) and dipyramids (**4**), as well as irregular planar hexagonal prisms (**5**).

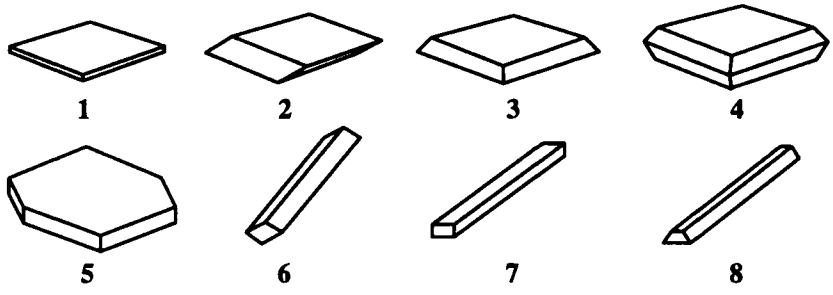

FIGURE 4 Crystal morphologies obtained in the BETS/$GaCl_4^-$ electrocrystallization experiments.

TABLE 3 X-ray and electrical transport characterization of the various crystal morphologies.

Morphology	Composition	Space Group	Conductive Properties
1	κ-$(BETS)_2GaCl_4$	Pnma	Semiconductor-metal T_{MI}~160K
2	κ-$(BETS)_2GaCl_4$	Pnma	Semiconductor-metal T_{MI}~160K
3	κ-$(BETS)_2GaCl_4$	Pnma	Semiconductor-metal T_{MI}~160K
4	κ-$(BETS)_2GaCl_4$	Pnma	Semiconductor-metal T_{MI}~160K
5	Twinned	—	Semiconductor-metal T_{MI} = 9K
6	λ-$(BETS)_2GaCl_4$	$P\bar{1}$	Superconductor T_c = 7.5K
7	κ'-$(BETS)_2GaCl_4$	C2/c	Semiconductor
8	Twinned	—	Superconductor T_c = 7.5K
9	α-$(BETS)_3GaCl_4$•TCE	Pnma	—

The acicular trapezoidal prisms (**8**) were only isolated from cells utilizing 1,1,1-TCE:5% ethanol. Morphologies **1-8** were characterized by X-ray crystallography and electrical transport measurements. When possible, room temperature unit cell parameters were determined for each morphology. Several crystals were examined for each crystal type. The unit cell experiments revealed that five of the morphologies were either κ- or λ-phases, two were twinned, and one (**7**) was a new material. The results of the X-ray studies and temperature dependent relative resistivity studies are provided in Table 3.

Morphologies **1-4** were κ-$(BETS)_2GaCl_4$; their unit cell parameters and resistivity-temperature profiles were identical. The use of gold paste instead of silver paste and slow cooling permitted reproducible κ-phase profiles to be obtained below 80 K (Figure 5). The lead resistances were still large and the data somewhat noisy, nevertheless. The resistive maximum varied, but was usually located at about 160 K. The crystals remained metallic to at least 2.5 K.

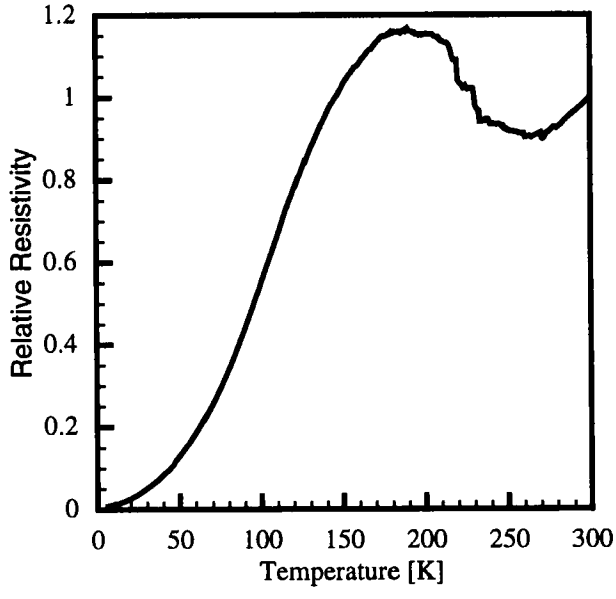

FIGURE 5 Relative resistivity of κ-$(BETS)_2GaCl_4$ in the ac plane as a function of temperature.

The needles with rhomboidal ends are the superconducting phase, λ-$(BETS)_2GaCl_4$. The needles with trapezoidal ends (**8**) were twinned and a structure determination was not attempted. Morphology **8** most likely possesses a λ-type

packing, since crystals of **8** had superconducting transitions similar to that of λ-$(BETS)_2GaCl_4$.

The needles with orthorhombic ends were a new semiconducting phase with a 2:1 stoichiometry and a kappa packing motif designated κ'. The kappa and the kappa prime salts crystallize in different space groups (Pnma and C2/c, respectively, Table 2). The slight differences in kappa and kappa prime packing are shown in Figures 6 and 7.

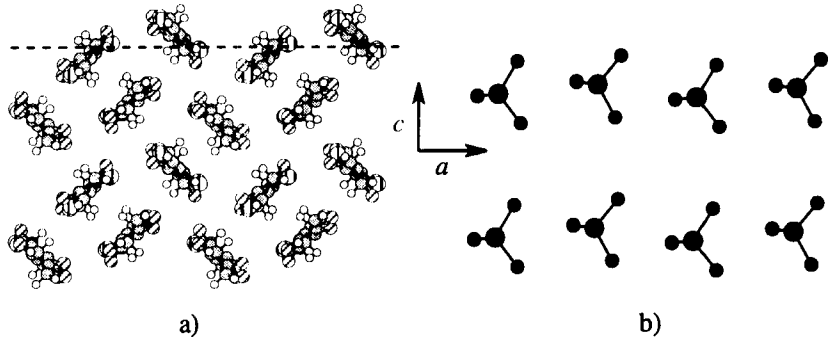

FIGURE 6 Cation (a) and anion (b) layers of κ-$(BETS)_2GaCl_4$.

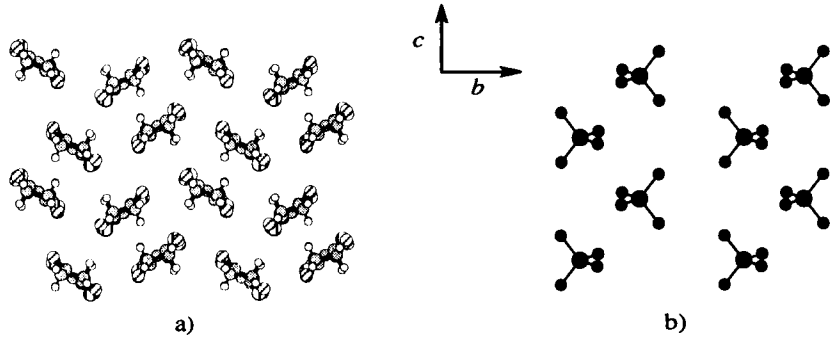

FIGURE 7 Cation (a) and anion (b) layers of κ'-$(BETS)_2GaCl_4$.

The final phase (**5**) was twinned; it was semiconducting to about 9 K, where the resistivity dropped monotonically to at least 4 K.

Although the study of the various phases derived from BETS and tetrabutylammonium tetrachlorogallate has yielded several new organic conductors and some interesting observations, it has not provided a new material with a T_c over 7.5 K. A variety of related studies are continuing in this system.

Supplementary Materials

Complete X-ray crystallographic data for all the structures discussed herein are deposited with the Indiana University Molecular Structure Center: http://www.iumsc.indiana.edu/.

Acknowledgments

Research at Indiana University was sponsored by the division of Materials Research of the National Science Foundation (DMR-9023347 and DMR-9414268) and the Air Force Office of Scientific Research, Directorate of Chemistry and Materials Science (F49620-92-J-0534). Work at Sandia National Laboratories was supported by the United States Department of Energy under contract DE-AC-94AL85000.

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