

## Arrhenius conduction restored by positional ordering of anions in the one-dimensional conductor (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub>

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The quasi-one-dimensional tetrathiafulvalenium conductor with mixed inorganic anions of nonstoichiometric composition (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> was obtained by electrochemical crystallization. It was found to have a tetragonal lattice with  $a=b=11.2043(6)$  Å,  $c=3.623(1)$  Å, and  $Z=2$ . Analysis of the crystal structure assuming the space group  $P4_2/mnm$  revealed that the TTF sublattice is isostructural to those of the other TTF conductors with mixed anions. Anions were found to be positionally ordered with fourfold periodicity with a dimension of  $c'=25.03(1)$  Å, but compositionally disordered giving very weak Bragg reflections at  $0.566c'$  in the oscillation photograph. The room-temperature conductivity along the stacks was 12–110 S/cm with an average value of  $43\pm 30$  S/cm. Below 110 K, it showed an Arrhenius conduction with a well-defined activation energy of 60 meV. This temperature dependence is contrary to those displayed by all the other TTF conductors of the same series which are classified as one-dimensional variable-range-hopping conductors. The Arrhenius conduction of (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> supports the point of view of disorder theory which attributes the origin of the variable-range-hopping conduction to the disorder of the structure. [S0163-1829(96)07033-6]

**Introduction.** The nature of the conduction and the composition-structural relations of the low-dimensional conductors has been a subject of great interest for the last two decades since the discovery of the highly conducting tetrathiafulvalene (TTF) tetracyanoquinodimethane (TCNQ) complex.<sup>1-3</sup> It has been shown that there is a competition between two sublattices for the dominant crystal structure. This is particularly prominent in the one-dimensional (1D) conductors typified by TTF halides and metal chain compounds. They have a simple composition with a single conducting chain, highly symmetric crystal packing, and show various degrees of structural instabilities.

A renewed interest in the novel features of TTF-based conductors was initiated when another series of conductors was reported. They have compositions of (TTF)(X)<sub>x</sub>(Cl)<sub>y</sub> ( $X=\text{ClO}_4$ ,<sup>4</sup>  $\text{BF}_4$ ,<sup>5</sup>  $\text{SCN}$ ,<sup>5</sup>  $\text{Br}$ ,<sup>6</sup> and  $\text{I}$ ,<sup>6</sup>  $x+y<1$ ) and nonstoichiometric mixed anions are fully disordered in the channel formed by the surrounding TTF stacks. Moreover, their temperature dependences of conductivity are all in accordance with the Mott's 1D variable-range-hopping (VRH) model.<sup>7</sup> It has been suggested through theoretical considerations that the positional disorder of mixed anions might induce localization of wave functions over TTF chains leading to VRH conduction. The present 1D conductor (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> was found to exhibit an Arrhenius conduction having a positionally ordered but compositionally disordered anion sublattice.

**Experimental.** 0.1 g of TTF (Tokyo Kasei, GR), 0.176 g of tetrabutylammonium (TBA) thiocyanate (Aldrich Chem.) and 0.178 g of tetrabutylammonium nitrate (Kanto Chem., GR) were dissolved in 65 ml of acetonitrile (Nacalai Tesque, liquid-chromato grade) and placed in an H-shaped cell equipped with air-tight caps and platinum rod electrodes of 1 mm diameter separated into two compartments by a glass

frit. The solution was electrolyzed galvanostatically at  $\sim 2$   $\mu\text{A}$ . The crystals were harvested after three or four weeks of electrolysis, washed with acetonitrile, dried in vacuum, and stored in a desiccator over silica gel. The crystals were obtained as bundles of black needles with a rectangular cross section of 0.06–0.21 mm wide and 1.28–4.07 mm long. Analytical results for the sample are given below:

Calc.	C, 32.67 H, 1.70 N, 3.36 O, 2.02 S, 60.26%
Found	C, 32.72 H, 1.74 N, 3.21 O, 1.92 S, 60.40%*

\*The oxygen content was determined by the difference.

The density of the crystals was determined as 1.75(1) g/cm<sup>3</sup> by flotation in an aqueous solution of zinc bromide. A black block crystal of (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> having approximate dimensions of  $0.3\times 0.4\times 0.5$  mm<sup>3</sup> was mounted on a glass fiber. All intensity measurements were made on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a 12 kW rotating anode generator. A total of 870 reflections were collected. The structure of the cation sublattice was determined separately from the anion structure by heavy-atom Patterson methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The oscillation photograph was taken using a MAC Science M03X x-ray generator of 3 kW with Cu  $K\alpha$  radiation.

Conventional four-probe dc conductivity measurements were carried out for single crystals in the temperature range of 50–300 K. The conductivity was examined using more than ten bundles of single crystals of sufficient strength for the measurements. Details of the measurements have been given in our previous report.<sup>4</sup>

**Results.** The chloride-free solvent containing two kinds of

TABLE I. Fractional atomic coordinates and thermal parameters.

Atom	X	Y	Z	Beqv <sup>d</sup> (Å <sup>2</sup> )
S 1	0.194 31(7)	-0.009 77(7)	0.0000 <sup>a</sup>	4.40(2)
C 1	0.043 1(2)	-0.043 1 <sup>a</sup>	0.0000 <sup>a</sup>	3.42(3)
C 2	0.239 6(3)	-0.157 5(3)	0.0000 <sup>a</sup>	5.32(7)
H(C2)	0.313(4)	-0.165(4)	0.0000 <sup>a</sup>	6.3(8)
SCN	0.0 <sup>a</sup>	-0.5 <sup>a</sup>	(0~1.0) <sup>c</sup>	16.4 <sup>b</sup>

<sup>a</sup>Fixed.

<sup>b</sup>Isotropic temperature factor (Å<sup>2</sup>).

<sup>c</sup>Disordered along the *c* axis.

<sup>d</sup> $Beqv = 4(a^2B_{11} + b^2B_{22} + c^2B_{33} + 2abB_{12} \cos \gamma + 2bcB_{23} \cos \alpha + 2caB_{13} \cos \beta)/3$ .

anion sources was used to examine the possible preparation of mixed-anion TTF conductors. TTF(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> was obtained successfully by electrolysis from acetonitrile solution. Another mixed-anion TTF salt, TTF(SCN)<sub>0.12</sub>(Cl)<sub>0.56</sub>,<sup>8</sup> was obtained in a similar way. It has a different stoichiometry from TTF(SCN)<sub>0.09</sub>(Cl)<sub>0.66</sub>,<sup>5</sup> which was prepared from a 1,2-dichloroethane solution by incorporating chloride through the decomposition of the solvent.<sup>4</sup>

X-ray photography revealed neither additional weak satellite-type reflection, indicating the existence of lattice super structure, nor a diffuse scattering line. It gave several very weak Bragg reflection spots on the oscillation photograph at 0.566C\* between the zeroth and first layer lines of the TTF sublattice.

The unit cell based upon the TTF sublattice corresponded to a primitive tetragonal cell (Laue class: 4/*mmm*) with dimensions:  $a = 11.2043(6)$  Å,  $c = 3.623(1)$  Å,  $V = 454.79(7)$  Å<sup>3</sup>. For  $Z = 2$  and F.W. (formula weight) = 237.86, the calculated density is 1.737 g/cm<sup>3</sup>, while the observed density is 1.75(1) g/cm<sup>3</sup>. Based on the systematic absence of  $0kl:k+l=2n+1$ , and  $h0l:h+l=2n+1$ , packing considerations, a statistical analysis of the intensity distribution, and the successful determination and refinement of the structure, the space group was determined to be  $P4_2/mnm$  (No. 136). The final cycle of full matrix least-squares refinement was based on 299 observed reflections [ $I > 3.00\sigma(I)$ ] and 20 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.035$  and  $R_w = 0.054$ , respectively.

Anionic lattice constants were determined from 18 reflections as  $a = 11.19(2)$  Å and  $c' = 25.11(4)$  Å. The structural analysis of the anion sublattice was not possible due to the very weak and few reflections observed. The anion lattice has a fourfold periodicity with an average anion spacing of 6.28(1) Å. Table I contains the fractional parameters for the

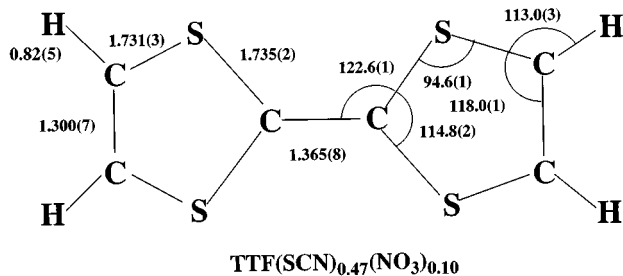


FIG. 1. Molecular geometry (Å and deg) of the TTF radical cations.

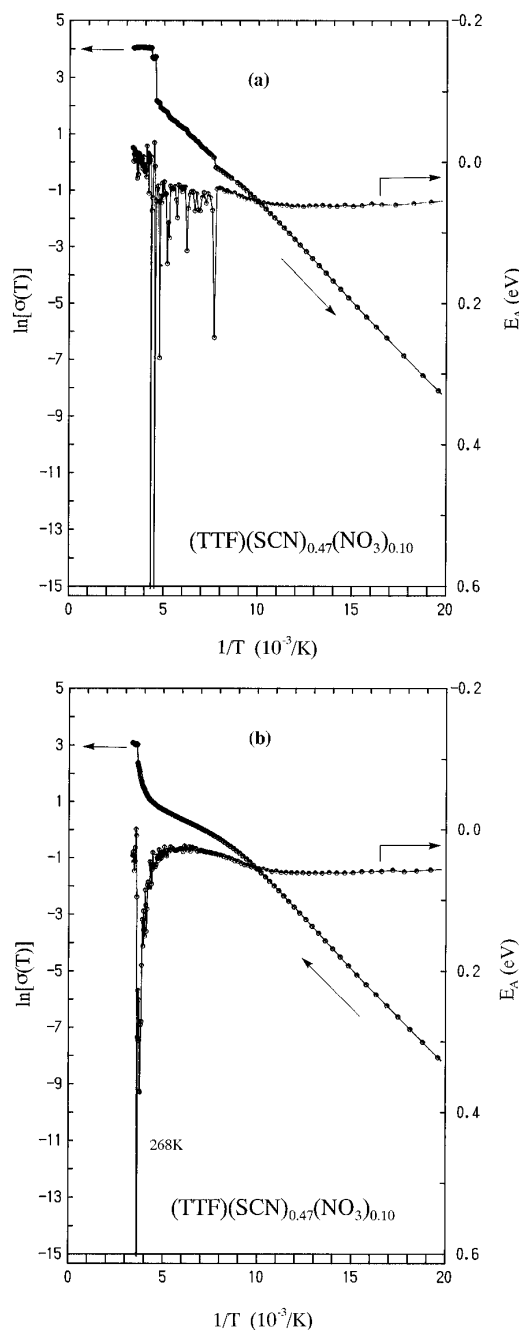


FIG. 2. Temperature dependence of the four-probe dc conductivity  $\sigma(T)$  and its derivative plot versus inverse temperature of (a) pristine TTF(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> during the first cooling process, (b) TTF(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> during the heating process. The arrow indicates the direction of the thermal process.

TTF radical and anion in the cell. The molecular geometry of the TTF radical is shown in Fig. 1.

The room-temperature conductivity of the single crystals lay in the 12–110 S/cm range with an average value of  $43 \pm 30$  S/cm. The conductivity is comparable with the reported values of other mixed-anion TTF conductors.<sup>4,5</sup> It is one and a half order of magnitude smaller than the values for TTF conductors having a single anion. This big conductivity drop is thought to be caused by the anion mixing.

The temperature dependence of the conductivity of a sample was observed in the temperature range of 50–300 K as illustrated in Fig. 2(a). The figure shows sudden conduc-

tivity drops at two or three temperatures below room temperature down to 145 K and then goes linearly down to 50 K. This is the first Arrhenius conduction found so far among this series of mixed-anion TTF salts. The irregular thermal behavior below room temperature disappears when the thermal cycle is reversed as is illustrated in Fig. 2(b), and never appears again in the further cycles. All samples examined showed this hysteresislike behavior during the first thermal cycle. After experiencing low temperatures such as 50 K, the samples undergo a sharp metal-insulator transition at  $269 \pm 6$  K, and behave as semiconductors with a well-defined activation energy of 60 meV.

*Discussion.* All the crystals of mixed-anion TTF conductor obtained so far contain chloride as a common partner of the anions. It is supported to be produced and incorporated into crystal during electrolysis by the decomposition of 1,2-dichloroethane used as a solvent for the electrochemical crystallization.<sup>4</sup>

The mixed-anion TTF compound (TTF) (SCN)<sub>0.47</sub> (NO<sub>3</sub>)<sub>0.10</sub> was successfully obtained from acetonitrile solution containing two kinds of anion sources TBA(SCN) and TBA(NO<sub>3</sub>). This method was later proved to be applicable to prepare several more mixed-anion TTF compounds by combining anion sources of appropriate size and shape. They are (TTF)(SCN)<sub>0.12</sub>(Cl)<sub>0.56</sub>,<sup>8</sup> (TTF)(SCN)<sub>0.09</sub>(Br)<sub>0.59</sub>,<sup>8</sup> and (TTF)(SCN)<sub>0.56</sub>(ClO<sub>4</sub>)<sub>0.01</sub>.<sup>8</sup> The characteristics of these compounds will be reported elsewhere.

Years ago, Somoano *et al.* reported on TTF(SCN)<sub>0.58</sub>,<sup>9</sup> which has an oxidation state of 0.58. This value is very close to 0.57 found for (TTF)(SCN)<sub>0.47</sub> (NO<sub>3</sub>)<sub>0.10</sub> and (TTF)(SCN)<sub>0.56</sub>(ClO<sub>4</sub>)<sub>0.01</sub>.<sup>8</sup> Presumably the thiocyanate ion is more dominant than the other partner of the anion pair in determining the anion stoichiometry when it is paired to form a mixed-anion salt.

The thermal hysteresis of the conductivity has been observed in several compounds containing SCN anions such as TTF(SCN)<sub>0.57</sub>,<sup>10</sup> TTF(SCN)<sub>0.09</sub> (Cl)<sub>0.66</sub>,<sup>5</sup> and TTF(SCN)<sub>0.56</sub>(ClO<sub>4</sub>)<sub>0.01</sub>.<sup>8</sup> It seems most probable that the SCN ion is responsible for this thermal behavior in these conductors because a linear ion has more freedom of movement than spherically symmetric ions and would take a much longer time to relax in a lattice site. In the case of a pristine crystal of (TTF)(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub>, it may be in some of the quasistable states, and may go to a stable state upon the first cooling. The  $T_{MI}$  of this compound is the highest temperature reported so far for this series of conductors. This implies that a relatively large interchain interaction is taking place intermediated by the anion lattice as was discussed in our previous report.<sup>11</sup>

To date, all of the examined mixed-anion TTF conductors have behaved according to Mott's VRH model and three of them have been proved to possess completely disordered anion structures.<sup>4,5</sup> The temperature dependence of the conductivity ( $\sigma$ ) in the VRH model is expressed as  $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/n}]$ , where  $\sigma_0$  is the conductivity at  $T_0$  and these parameters depend on the density of states and orbital exponent of the localized wave function at the Fermi level.  $n$  is an integer determining the  $(n-1)$  dimensionality of the conduction. Assuming this model for the 1D TTF conductors with mixed anions, their conduction data are well described by a  $T^{-1/2}$  temperature dependence. Because of the nature of

the temperature dependence of conductivity, the origin of the hopping conduction has been considered as intrinsic rather than due to impurities or lattice imperfection. Thus, it is thought to be due to the disordered structure contained in the crystal. As has been expected from our previous study and observations, when anions form an ordered lattice, the conductivity might obey an Arrhenius relation with temperature. Actually, this was found to be true as is described below.

The TTF cation radical formed a stable sublattice stacked in an eclipsed column. The molecular plane lay in the  $ab$  plane and the sulfur atomic orbitals of the TTF overlapped face to face with each other with those of the adjacent radicals in the stack. The molecular plane had a repeating distance of 3.623(1) Å. This is short enough for electron conduction to take place through the TTF columns. Other salts had a little bit smaller averaged interplanar spacing of 3.595–3.608 Å. It stays almost constant although the formal charge on the radical varies from +0.56 to +0.75.

A series of very weak spots along the  $c$  axis at  $0.566^*C$  on the oscillation photograph revealed the development of ordered structure of the anion sublattice. 18 reflections due to anion lattice were observed by AFC7R. Detailed analysis of a layer line at  $0.577C^*$  revealed that the average anion spacing is 6.258(3) Å. This positional ratio is nearly equal within the experimental error to the degree of oxidation, 0.57, obtained from the elemental analysis and cross checked by crystal density measurement. Thus the chemical composition for this crystal is in good agreement with the x-ray prediction.

Along the  $c$  axis, the anion lattice has a fourfold periodicity with repeating distance of 25.02(1) Å which coincides with seven repeat units length of the TTF column [i.e., 25.361(7) Å]. This unusual fourfold periodicity of the anion sublattice is most probably induced by the periodical interaction between TTF and the anion with every seven repeat units of TTF spacing as is revealed from its commensurate stoichiometry of  $4/7 (=0.571)$ .

The anion sublattice is composed of 82.5% SCN and 17.5% NO<sub>3</sub><sup>-</sup>. Thus the repeating unit should contain 3.3 SCN and 0.7 NO<sub>3</sub><sup>-</sup>. This is apparently impossible for one repeating unit. Therefore, the NO<sub>3</sub> anions should be randomly distributed among the anion sites in the above ratio while the whole anion sites are well ordered positionally in fourfold.

This way of anion packing can be described by analogy with the prototype compound (TTF)<sub>12</sub>(SCN)<sub>7</sub>.<sup>9</sup> It has almost the same oxidation state of  $7/12 (=0.583)$  as the present mixed-anion salt and has a fully ordered anion sublattice with an anion spacing of 6.15(3) Å. Starting from TTF(SCN)<sub>0.58</sub>, our salt TTF(SCN)<sub>0.47</sub>(NO<sub>3</sub>)<sub>0.10</sub> can be constructed by replacing a part of the SCN anion with NO<sub>3</sub> up to 17.5% of the number of ions, while the anion lattice still keeps the positional ordering.

The effect of anion replacement upon crystal structure seems to be minor. Nitrate has 32 electrons while the replaced thiocyanate has 30 and the increase in electron density among the anion lattice associated with the replacement would not be large enough to be detected during structural analysis by a conventional diffraction technique.<sup>12</sup> The effect of compositional disorder might have been smeared out by positional ordering of the anion sublattice. Therefore, it can be said that the anion lattice in this crystal is positionally

ordered but compositionally disordered. Yet the effect of this positional ordering of the anion sublattice is big enough to restore Arrhenius conduction from Mott's VRH conduction where the anions are fully disordered.

A replacement of the constituents at crystal lattice sites with different atoms or molecules is commonly seen in solid solution or alloys. The concept of "alloying" is sometimes applied to organic conductive crystals and resultant material is termed a "molecular alloy" such as  $(TSeF)_x(TTF)_{1-x}(TCNQ)$  (Ref. 13) (where TSeF is tetrasetenafulvalene and  $x=0-1.0$ ) or  $(Phen)_x(NMP)_{1-x}(TCNQ)$  (Ref. 14) (where Phen is phenazine and NMP is N-methylphenazinium and  $x=0-0.46$ ). The compositional disorder was intentionally introduced into the NMP conducting chain and the nonintegral stoichiometry  $x$  can be varied continuously in a certain range. Only fixed anion stoichiometry could be seen in case of the mixed-anion salts.

All the mixed-anion TTF salts studied so far have positionally disordered anion structure and exhibited 1D VRH conduction without exception. Reconsidering the reported data of  $TTF(I)_{0.71}$ ,<sup>15</sup>  $TTF(Br)_{0.76}$ ,<sup>16</sup>  $TTF(SCN)_{0.58}$ ,<sup>10</sup> and  $TTF(SeCN)_{0.58}$ ,<sup>10</sup> we can recognize that they all have ordered anion structures and exhibit an Arrhenius-type temperature dependence of dc conductivity. Very similarly, the present mixed-anion conductor  $(TTF)(SCN)_{0.47}(NO_3)_{0.10}$  obeys the Arrhenius law but not the VRH model. These facts suggest that a 1D conductor exhibits Arrhenius conduction when it has an ordered anion lattice. Actually the crystals possess an ordered anion sublattice as has been expected from the above-mentioned experimental data. All these facts imply that anion positional ordering plays a decisive role in the conduction process and this is in good accordance with the disorder theory for VRH conduction applied so far to low-dimensional or amorphous semiconductors.<sup>17</sup>

The positional ordering of anions induces the delocalization of conduction electrons leading to the Arrhenius conduction even when the anion sublattice is compositionally disordered. It is surprising to note that even such an incomplete ordering is enough to restore the Arrhenius conduction as is in a fully ordered crystal lattice. The primary importance of the positional ordering over composi-

tional ordering was also recognized in the study on  $(Phen)_x(NMP)_{1-x}(TCNQ)$  where the positional order of the cation sublattice is well preserved and the compositional disorder plays a secondary role.<sup>13</sup> The conduction electrons on the TTF stacks seem to be more sensitive to the positional ordering of the anions than to the compositional ordering. This is reasonable if we note that the delocalized electrons on cation stacks see the periodical potential exerted by the ordered anion lattice rather than the minor difference in anion species between the sites.

Electronic states in disordered structures have been extensively discussed by Anderson,<sup>18</sup> Mott,<sup>7</sup> Cohen and co-workers,<sup>19,20</sup> and Ambegaokar, Halperin, and Langer.<sup>21</sup> Their main conclusion is that the random potential due to disordered structure produces localization of wave functions near the Fermi level in the forbidden band inducing the variable-range-hopping conduction of the system. This theory was successfully applied to amorphous semiconductors and several 1D conductors by Bloch, Weisman, and Varma.<sup>17</sup> This so-called "disorder theory" has been found to be also applicable to the mixed-anion TTF conductors.<sup>4,5</sup> The consistent applicability of the VRH model to this conductor system convinced us that the disorder structure is the origin of the wave-function localization, and therefore, of hopping conduction. The present finding of the Arrhenius conduction in  $(TTF)(SCN)_{0.47}(NO_3)_{0.10}$  is further experimental support for the disorder theory of VRH conduction.

**Conclusion.** A quasi-one-dimensional tetrathiafulvalenium conductor with mixed inorganic anions  $(TTF)(SCN)_{0.47}(NO_3)_{0.10}$  was obtained by electrochemical crystallization. It was found that anions are positionally ordered with fourfold periodicity, but are disordered compositionally. Its conductivity behaved with variable temperature according to the Arrhenius law with a well-defined activation energy. This is quite contrary to the 1D Mott's VRH conduction displayed by other compounds of the same series with fully disordered anion structure. This illustrates the decisive role of anion positional ordering on the electrical conduction of the TTF chain. When an anion is positionally ordered, the conduction obeys the Arrhenius law, or if it is disordered it obeys the VRH model.

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<sup>12</sup>Later it was found that another new conductor  $(TTF)(SCN)_{0.56}(ClO_4)_{0.01}$  has two kinds of superstructures which might be originated by both components of anion lattice. This was revealed on an oscillation photograph as very weak

spots among Bragg reflections due to the averaged TTF lattice structure.

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