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## THERMAL EXPANSION OF SOME MORPHOLINIUM-TCNQ SALTS IN STACK DIRECTION.

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### ABSTRACT

Data on the thermal expansion coefficients of some Morpholinium-TCNQ salts are presented. Measurements were carried out with the help of a Michelson interferometer.

### 1. INTRODUCTION

Compounds of Morpholinium derivatives and Tetracyanoquinodimethane(TCNQ) form crystalline, organic, quasi-one-dimensional electrical conductors. The conductivity of these conductors is anisotropic: electrons (and holes) can move more freely along the stacks of TCNQ molecules than in other directions. The transfer integral affects the electrical conductivity and strongly depends on the intermolecular distance. Therefore information on the thermal expansion in the stack direction is important for a better understanding of the temperature dependence of the conductivity in these materials<sup>1</sup>. The thermal expansion measurements reported in ref.4 were carried out by x-ray diffraction. Such measurements provide information on the temperature dependence of the crystallographic unit cell.

The accuracy of this method is limited by the fact that the effect of thermal expansion on the unit cell is relatively small. Hence the expansion coefficients are obtained by observing the difference in the unit cell parameters at two widely different temperatures.

In the present paper we present the result of an interferometric determination of the thermal expansion coefficient. This method has the advantage that it is much more sensitive; hence thermal expansion can be studied in a rather narrow temperature interval. The interferometric method differs from the x-ray experiment in that it measures bulk expansion rather than the change in the crystallographic unit cell. In our experiment we have only studied the thermal expansion in the direction of the TCNQ stacks.

## 2. EXPERIMENTS AND RESULTS

Typical crystal dimensions are  $3 \times 0.2 \times 0.2 \text{ mm}^3$ . On top of these crystals a thin mirror,  $3 \times 3 \times 0.15 \text{ mm}^3$ , was glued. The bottom of the crystal was glued on a mirror, the temperature of which was controlled with a Peltier element and measured with a Platinum resistance. Either of these mirrors served as one of the two mirrors in a Michelson interferometer. The translation of both mirrors was measured as a function of temperature and the difference in translation yields the thermal expansion of the crystal. The thermal expansion coefficient was measured in the temperature range from 270 to 330 K. From a check of our experimental accuracy with a test sample of copper with a length of 12 mm we obtained a thermal expansion coefficient of

$15.9 \pm 1.0 \cdot 10^{-6} \text{ K}^{-1}$  in agreement with the value of  $16.6 \cdot 10^{-6} \text{ K}^{-1}$  quoted in the literature<sup>2</sup>. The results of the measurements of the thermal expansion coefficients of some Morpholinium TCNQ salts are given in the table. In the temperature range considered these values are independent of temperature.

TABLE:

<u>material:</u>	<u>thermal expansion</u> <u>coefficient</u>
Methyl Ethyl Morph.(TCNQ) <sub>1</sub>	$1.16 \pm 0.09 \cdot 10^{-4} \text{ K}^{-1}$
Methyl Ethyl Morph.(TCNQ) <sub>2</sub>	$0.91 \pm 0.06 \cdot 10^{-4} \text{ K}^{-1}$
Methyl Ethyl thio Morph.(TCNQ) <sub>2</sub>	$1.44 \pm 0.13 \cdot 10^{-4} \text{ K}^{-1}$
Methyl norm.Butyl Morph.(TCNQ) <sub>2</sub>	$1.90 \pm 0.12 \cdot 10^{-4} \text{ K}^{-1}$
Hydrogen norm.Butyl Morph.(TCNQ) <sub>2</sub>	$1.08 \pm 0.12 \cdot 10^{-4} \text{ K}^{-1}$
Hydrogen norm.Butyl thio Morph.(TCNQ) <sub>2</sub>	$0.89 \pm 0.08 \cdot 10^{-4} \text{ K}^{-1}$

Note that these are relatively large thermal expansion coefficient, typical a factor 100 larger than for copper. Methyl Ethyl Morpholinium (TCNQ)<sub>2</sub> showed a phase-transition at about 333K with a hysteresis of 2K. in good agreement with ref. 3. For two of the compounds studied X-ray diffraction data are available <sup>4</sup>:

Methyl Ethyl Morph. (TCNQ) <sub>1</sub>	1.07	$10^{-4} \text{ K}^{-1}$
Methyl Ethyl thio Morph.(TCNQ) <sub>2</sub>	1.08	$10^{-4} \text{ K}^{-1}$

in fair agreement with our measurements. The deviation in Methyl Ethyl thio Morpholinium (TCNQ)<sub>2</sub> could arise from crystal defects not affecting X-ray measurements.

factor two the same thermal expansion coefficient in the stack direction and this holds true also for<sup>5</sup> TTF-TCNQ ( $1.5 \cdot 10^{-4} \text{ K}^{-1}$ ) and another charge transfer salt (TMTSF)<sub>2</sub>FSO<sub>3</sub> ( $1.2 \pm 0.1 \cdot 10^{-4} \text{ K}^{-1}$ )

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