Order-Disorder Phase Transition in a Triiodide Chain Compound: DIPSø$_4$ (I$_3$)$_{0.76}$

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ORDER-DISORDER PHASE TRANSITION IN A TRIIODIDE CHAIN
COMPOUND : DIPSϕ_4 $(I_3)_{0.76}$

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Abstract   The ordering process of triiodide chains in the or-
ganic conductor DIPSϕ_4 $(I_3)_{0.76}$ has been studied by X ray
scattering.

STRUCTURE OF THE COMPOUND

DIPS$\phi_4(I_3)_{0.76}$ is an organic conductor belonging to the radical-ion
family[1]. It is grown by the direct oxydation of DIPSϕ_4 molecules by
iodine in a solvent.
DIPSϕ_4 columns running along the c-axis delimit parallel channels
filled with I_3^- anions (see below).

Crystal system : tetragonal

Space group   : P $4\bar{b}2$

Unit cell a   : 19.74 Å
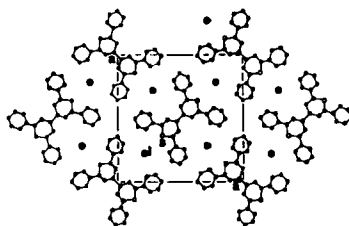
           c   : 3.721 Å

FIGURE 1. Projection of the structure along the c axis[2]

STRUCTURE OF THE TRIIODIDE CHAINS AT ROOM TEMPERATURE

At room temperature X ray photographs reveal intense diffuse lines
perpendicular to the c axis[3] . It has been shown that these lines

were due to the disordered triiodide channels. Furthermore they present only small modulations, showing that the different I_3^- chains are very weakly correlated[3]. Fig. 2-a represents a microdensitometer scan of a photograph along the c-axis (l index). We see well defined peaks which broaden as l^2 with increasing line index l. This broadening can be viewed as resulting from 1D liquid fluctuations; this is also encountered in other triiodide compounds[4]. A model in which the interactions between I_3^- units in a channel are assumed to be harmonic and between first neighbours has been used[5-6]. As can be seen on Fig.2-b, it accounts relatively well for the observed intensity. The additional lines (arrows) have been interpreted as a modulation of the I_3^- chains by the host lattice.

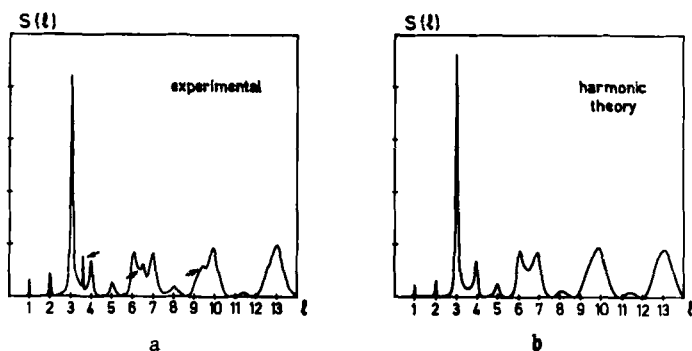FIGURE 2.a. : Microdensitometer reading along the c axis. (corrected for absorption and polarization)

FIGURE 2.b. : Theoretical intensity (harmonic model) corrected for the molecular factor of I_3^-.

EFFECT OF THE TEMPERATURE

As the temperature is lowered the first diffuse line becomes clearly modulated, this means that lateral correlations between triiodide chains develop. These precursor phenomena condense into

Bragg spots at about T_c = 185 K. Thus below T_c triiodide chains
are laterally and longitudinally long-range ordered.

STUDY OF THE ORDERING PROCESS

The ordering process may be described by the Bragg spots appearing
on the diffuse lines : the intensity of a Bragg spot appearing
on the lth line is proportional to the square of the lth Fourier
component of the mass-density. In Fig. 3 we have plotted the in-
tensity of Bragg spots appearing on the first four lines (1 =
1 to 4).

a   b
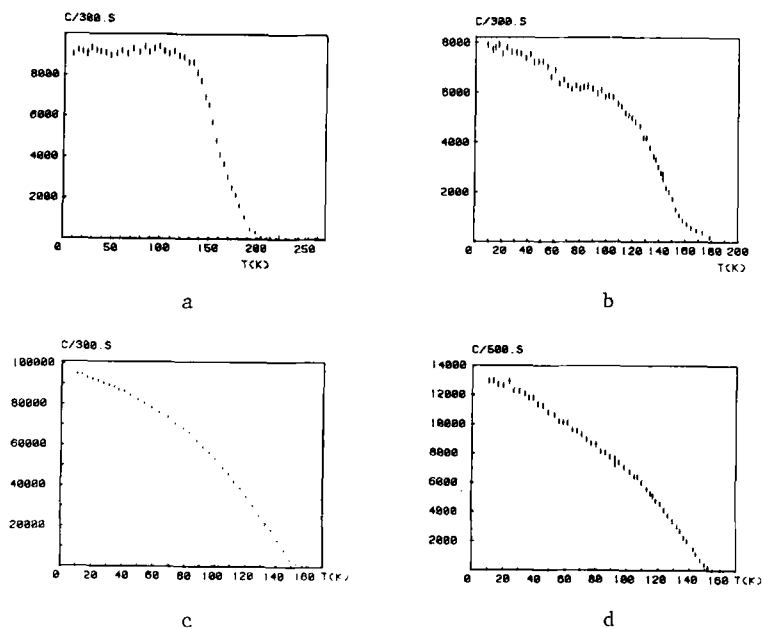

c   d

FIGURE 3.a.b.c.d. Intensity of Bragg spots appearing respectively
on line 1, 2, 3, 4 versus temperature.

DISCUSSION

We see that Bragg spots develop first on the first line, then on
the second one and the third and fourth ones; the last two inten-
sities displaying pratically the same behaviour. Furthermore the
intensity of $\ell = 1$ Bragg spots saturates at about 100 K. A mean
field theory of this transition, using the harmonic model has
been developped by V.J. Emery and J.D. Axe[5]. It accounts well for
the progressive apparition of the Bragg spots with increasing
line index but not for the saturation of the $\ell = 1$ Bragg spots
and the rapid growth of the others. A possible explanation could
be in the broad conductor/semi-conductor phase transition that
occurs at about T_c[7]. As the conductivity of the $DIPS\phi_4$ columns
diminishes, the screening between I_3^- chains decreases, which
increases the coupling between them. This could lead to the obser-
ved avalanche effect.

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