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ANION ORDERING AND ATOMIC VIBRATIONS IN $(TMTSF)_2ClO_4$

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Abstract - We report the first observation of the specific heat anomaly associated with anion ordering in $(TMTSF)_2ClO_4$. The phase transition analyse reveals a configuration entropy R Log (2) which can be reduced by 20% on fast cooled sample. The low temperature lattice specific-heat deviate strongly from the prediction of a 3D debye model.

INTRODUCTION

Earlier studies of quasi one dimensional conductors have shown that generally a phase transition transforms the high temperature conducting material into a low temperature insulator. In the two-chain charge transfer salts as TTF-TCNQ, instabilities of the electronic gas occur at $2k_F$, where k_F is the one dimensional Fermi level wave vector. These instabilities lead with the help of electron-phonon coupling to the well known Peierls transition. The driving force for this process is the minimisation of the electronic free energy.

In many one chain organic conductors one observe several kinds of phase transition. Three classes of low temperature ground states are observed in the group of isomorphous organic conductor $(TMTSF)_2X$: non magnetic semiconductor ($X = ReO_4$), antiferromagnetism ($X = PF_6$) and superconductivity ($X = ClO_4$). For this group, the Peierls process is not the unique driving force and the phase transitions involve an ordering and displacement of the anions as well as a $2k_F$ distortion along the one-dimensional axis a.

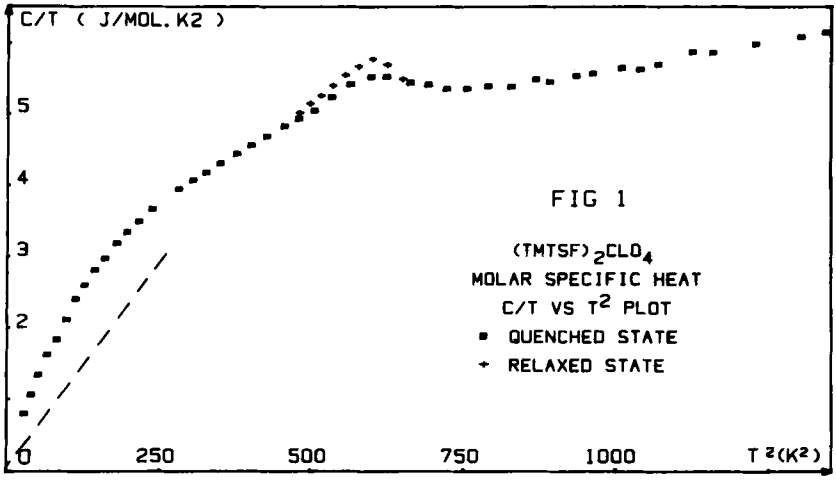
The crystal structure of these salts is made from stacks along the a-axis of flat organic molecules arranged in sheets and separated by (a,b) planes of anions X. These anions are located at inversion center in the $P\bar{1}$ space group,[1] for the non centrosymme-

tric anionsas ClO_4 or ReO_4 this implies two non-equivalent orientations and an associated configuration entropy. At room temperature anions are disordered and a possible ordering may occur as the temperature is decrease. In the ClO_4 compound it has been shown that the low temperature ground state was strongly affected by the cooling rate around 20 K. Fast cooling of the sample suppresses superconductivity [2] and stabilizes an antiferromagnetic state.[3] This phenomenon is fully reversible and superconductivity can be restored by heating above 30 K and subsequent slow cooling. The electronic transport has been measured in this temperature range and a change of slope is observed at 24 K.[4] Diffuse X-ray scattering studies reveal at the same temperature the formation of a low temperature superstructure which may involve an ordering of the ClO_4 anions.[5] It must be noted that the wave vector of the superstructure $q = (0,1/2,0)$ does not change the periodicity in the stacking direction. This implies a more subtil connection between the structural instability and the electronic ground state that a simple one dimensional Peierls distortion. In view of this we thought it is worthwhile to investigate the thermodynamical properties of the compound in this temperature range in order to establish the exact nature of this phase transition.

The specific heat results, corrected from addenda, are presented on Fig. 1. The molar specific heat (one mole is $(TMTSF)_2ClO_4$ time the Avogadro number) is presented as C/T v.s. T^2. The dashed line is a fit to our low temperature data, $T < 2$ K, reported in ref. 6. In this low temperature range the specific heat obeys the classical relation $C = \gamma T + \beta T^3$. The resulting Debye temperature $\theta_D = 80$ K has been calculated according to expression [1] :

$$\theta_D = \left[\frac{12\pi^4}{5}\ \frac{n}{\beta}\right]^{1/3} \qquad [1]$$

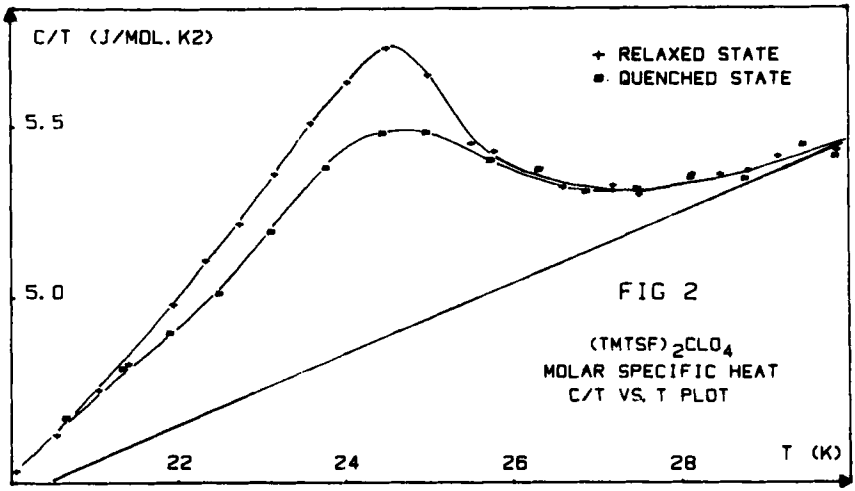
where $n = 3$ is assumed to be the number of vibrating units at low temperature. In general n can be taken equal to the number of heavy atoms plus the number of molecular groups that are assumed



rest. At higher temperature other contribution should be added ($n > 3$). With $n = 3$, the saturation of C_p amounts to $3\times(3R)$ which is much lower than the actually observed value at 35 K. In fact, there is no reason to assume that these materials should intrinsically display a simple Debye specific heat, in many complicated organic materials Debye temperature are exception and not the rule.[7] Nevertheless, this low temperature θ_D value can be compared with other organic compound and range in the lower observed values. Above 6 K we observe strong deviations from a T^3 law and the specific heat first increase faster than T^3 up to 12 K and then increase smoothly to reach a value $C_p \simeq 8\times(3R)$ at 35 K. This strong deviations are observed in low dimensional material like graphite, they are not observed in the one chain compound TTF-TCNQ where sound velocity measurements [8] indicate an elastically isotropic 3D solid.

ORDER-DISORDER TRANSITION

On Fig. 1 we observe around 24 K a bump on the specific heat curve; it represents 15 % of the total specific heat at this temperature. The experiments were performed on slow cooled sample (R; 0.1 kelvin /minute) and quenched sample (Q ; 10K/minute). The reduction of



is not fully ordered. On Figure 2, we present on an expended scale the molar specific heat in the critical region, in a C/T v.s. T plot. The solid line represents the regular specific heat fitted from the measured values above 30 K and below 15 K. The characteristic aspects of the specific heat anomalies are the following : the specific heat anomaly occurs at the same temperature T_c that the formation of the superstructure observed by X-ray scattering. By fitting the overall specific heat and the background we obtain the entropy involved in the transition $\Delta S = 4$ Joule/Mole.Kelvin. The specific heat does not diverge at T_c and critical fluctuations are observed up to 30 K. Assuming that the order-disorder transition is a configurational one where we go from a disordered state with n_1 possible configurations to an ordered state with n_2 ($n_2 < n_1$) configurations the change in entropy is :

$$\Delta S = R \, \mathrm{Ln} \, (n_1/n_2)$$

Our measured entropy difference yields a ratio of ion orientations of 2 per chloride ion in good agreement with crystallographic data. For the Q state the entropy ΔS is only 80 % of the R state one. In fact this value is an overestimate one of ΔS_Q because of a partial annealing during the measuring time.

These new results enrich our knowledge of the order-disorder phase transition in the $(TMTSF)_2$ family containing non centrosymmetric anions. They reveal unexpected low energy vibration modes which can be involved in superconducting pairing.

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