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NOISE IN HIGHLY CORRELATED COMMENSURATE CHARGE TRANSFER SALTS

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Résumé - Nous présentons les résultats d'une étude de la puissance de bruit pour le sel de transfert de charge commensurable avec une répulsion Coulomb forte. Un bruit proportionnel à la fréquence inverse (f^{-1}) est observé avec un courant croissant. Un bruit f^{-1} excessif est observé pour des échantillons qui ont été dopés pour produire des solitons. Le bruit proportionnel au courant et indépendant de la fréquence n'est pas observé.

Abstract - We present the results of a study of the frequency (f) dependent noise power for commensurate charge transer salts with strong coulomb repulsion. f^{-1} noise is observed with increasing currents. Excess f^{-1} noise is measured for samples which were chemically doped to form solitons. Frequency independent shot noise is not observed.

In recent work by Rice and Mele/1/ it was suggested that solitons with half-integer electron charge may exist in highly correlated 1:2 salts of tetracyanoquinodimethane, TCNQ. Similarly, Su and Schrieffer proposed/2/ that fractionally charged solitons of +ne/3, with n=1 or 2, may exist in one-third-filled band systems. It was further shown by Kivelson and Schrieffer/3/ that these fractional charges are sharp quantum observables and not merely the quantum average of integer charges. Earlier experiments/4/ verified the existence of soliton-like defect states in the one-quarter-filled highly correlated system (N-methyl phenazinium)$_x$(Phenazine)$_{1-x}$(TCNQ), (NMP)$_x$(Phen)$_{1-x}$(TCNQ), with $0.50 \leq x \leq 0.54$. Other studies /5/ have shown that (trimethylammonium)(Iodide)(TCNQ), $(NMe_3H)(I_3)_{1/3}(TCNQ)$, is a stoichiometric commensurate one-third-filled band system. The present study utilizes noise power measurements of the aforementioned compounds to study the role of solitons in transport and to probe for evidence of fractionally charged solitons.

The experimentally measured quantity is the total noise power per 1 Hz bandwidth (S_V^T) of the sample, including Johnson (S_V^J), flicker (S_V^f) and shot (S_V^S) noise contributions:

$$S_V^T = S_V^J + S_V^f + S_V^S. \qquad (1)$$

The first of these terms may be more explicitly written as,

$$S_V^J = 4\, k_B\, T\, R, \qquad (2)$$

where k_B is the Boltzmann constant, T the temperature in degrees Kelvin and R the sample resistance. The source of the second term in Equation 1 is not yet fully understood except in a few very specific cases/6/. However, it is typically written as,

$$S_V^f = K\,I^{\alpha} f^{-\beta}. \qquad (3)$$

Here K is a constant that in many cases may be shown to be volume dependent/6/, α and β are material dependent constants, with typical values $\alpha\sim 2$ and $0.6<\beta<1.5$. The final term in Eqn. 1, S_V^S, may be represented as,

$$S_V^S = 2\,e^{*}\,I\,R^2, \qquad (4)$$

where e* is the effective charge of the carriers involved in transport and I is the dc current through the sample. In the presence of recombination centers, or alternatively hopping sites, it has been shown/5/ that the shot noise term has an $f^{-\gamma}$ behaviour with $\gamma\sim 2$.

Measurements of the temperature dependent conductivity, $\sigma(T)$, were carried out using a four-probe configuration. The temperature dependence of the normalized conductivity, $\sigma_n(T) = \sigma(T)/\sigma\ (295K)$, for samples of $(NMe_3H)(I_3)_{1/3}(TCNQ)$ and $(NMP)_x(Phen)_{1-x}(TCNQ)$ with x = 0.51 and 0.53 is shown in Figure 1. The data have been renormalized to account for jumps in $\sigma_n(T)$ associated with the formation of microcracks within these fragile crystals during the course of the experiment. Comparison with earlier data/4,5/ show these crystals to be representative of this class of charge transfer salts. Figures 2 and 3 display the total noise power versus frequency for these same crystals at various current levels obtained at temperatures of approximately 100K using an HP3585A spectrum analyzer. The data was again taken using the standard four-probe technique. Expected values for the Johnson noise are indicated by the dashed lines. Several data points are below S_V^J due to the gain characteristics of the spectrum analyzer. After appropriate correction these points are above the calculated Johnson noise level.

$(NMe_3H)(I_3)_{1/3}(TCNQ)$ is a commensurate one-third-filled band system. Since it is stoichiometric with no chemical solitons, only thermally generated solitons are present. The S_V^J term is observed as expected and the flicker noise contribution increases with increasing current. No frequency independent shot noise is observed, although relaxation effects may result in a frequency dependent shot noise power indistinguishable from flicker noise. Since the data fits an f^{-1} form and is approximately quadratic in voltage, we may make use of the phenomenological equation for flicker noise developed by Hooge/7/,

$$S_V^H = 2.4 \times 10^{-3}\, V^2 / (N_c f). \qquad (5)$$

Here V is the applied voltage, N_c is the total number of carriers present in the sample and f is the frequency.

Through its dependence on the total number of charge carriers ($S^H \propto N_c^{-1}$), Hooge's equation implies that noise is a strictly bulk phenomenon. Using appropriate values for the unit cell volume/8/ and carrier concentration/9/, we obtain the curves in Figure 4. If it is assumed that the only charge carriers are electrons and holes thermally excited across the intrinsic 0.16 eV bandgap/4/ plus mobile thermal solitons, then the noise power predicted by Eqn. 5 is six orders of magnitude too small to account for the observed noise power. If it is postulated that the solitons are present and immobile, then they lead to changes in the number

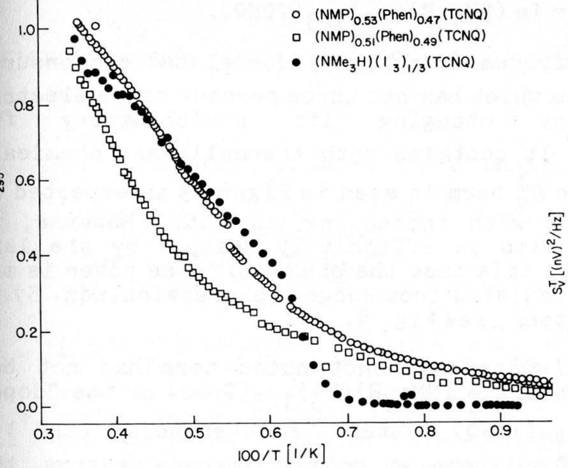

FIGURE 1: Normalized chain axis conductivity versus temperature for the three samples studied.

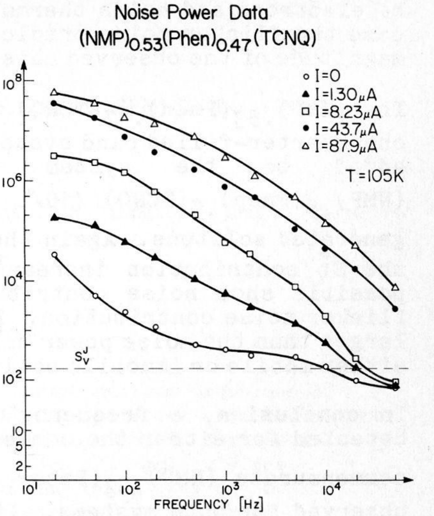

FIGURE 2: Total noise power versus frequency at various current levels for $(NMP)_{.53}(Phen)_{.47}(TCNQ)$.

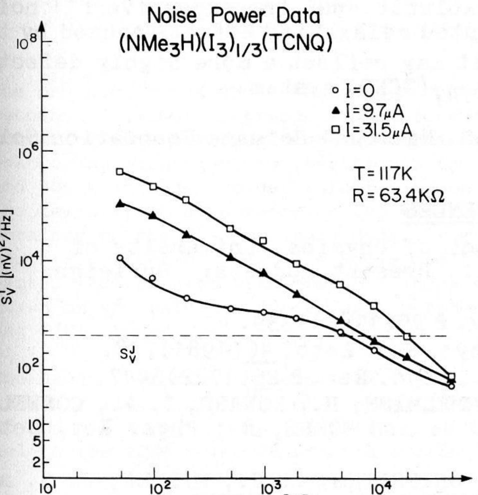

FIGURE 3: Total noise power versus frequency at various current levels for $(NMe_3H)(I_3)_{1/3}(TCNQ)$.

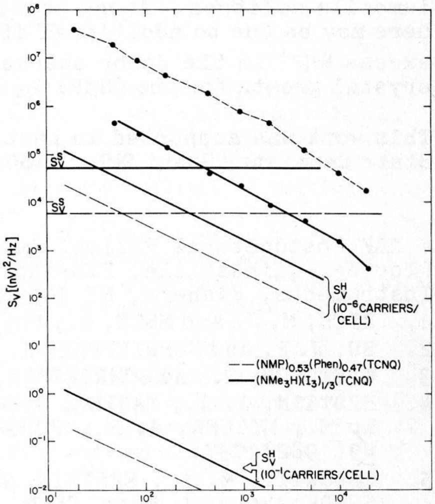

FIGURE 4: Noise power spectrum for $(NMP_{.53}(Phen)_{.47}(TCNQ)$ and $(NMe_3H)(I_3)_{1/3}(TCNQ)$ at currents of 43.7μA and 31.5μA respectively. Calculated values for the maximum expected shot noise and S_V^H for mobile (10^{-1} carriers/cell) and immobile solitons (10^{-6} carriers/cell) are also shown.

of electrons and holes thermally excited at a given temperature. In this case the flicker noise predicted by Hooge's expression is of the order of magnitude of the observed noise in $(NMe_3H)(I_3)_{1/3}(TCNQ)$.

The $(NMP)_{.53}(Phen)_{.47}(TCNQ)$ system is a highly correlated commensurate one-quarter-filled band system which has had three percent extra electrons added to the system by changing its stoichiometry from $(NMP)_{.5}(Phen)_{.5}(TCNQ)$ /10/. It contains both thermally and chemically generated solitons. Again the S_V^J term is seen in Figure 3 as expected and the S_V^f contribution increases with increasing current. However, any possible shot noise contribution is effectively swamped by the large flicker noise contribution. In this case the observed noise power is much larger than the noise power calculated from Hooge's expression(Eqn. 5) for either mobile or immobile solitons, see Fig. 4.

In conclusion, a frequency independent shot noise term has not been detected for either the commensurate $(NMe_3H)(I_3)_{1/3}(TCNQ)$ or the "doped" commensurate $(NMP)_{.53}(Phen)_{.47}(TCNQ)$ system. Flicker noise (f^{-1}) is observed for both systems. If solitons are mobile in these systems, then the flicker noise is six orders of magnitude too large to be explained by Hooge's bulk phenomena equation. If the thermally generated solitons are immobile in $(NMe_3H)(I_3)_{1/3}(TCNQ)$, then Hooge's expression for flicker noise is consistent with the observed magnitude of f^{-1} noise. For systems with chemically added solitons such as $(NMP)_{.53}(Phen)_{.47}$ (TCNQ), the observed flicker noise is in excess of Hooge's prediction with or without immobile solitons. Among possible explanations, the excessive f^{-1} noise here may be due to additional distributed relaxation effects caused by the excess NMP^+ in the donor stacks, or it may reflect a more highly defected crystal growth for the $(NMP)_{.53}(Phen)_{.47}(TCNQ)$ system.

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