TEMPERATURE DEPENDENCE OF NEAR INFRARED ABSORPTION OF TCNQ SALTS

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Theory of temperature dependent near-infrared absorption of TCNQ salts is developed. The electronic interactions are represented by extended Hubbard Hamiltonian. The theory is built on the concepts of effective operators and formalism of many-body perturbation theory. A special case corresponding to crystals of NaTCNQ above 348 K is studied in some detail.

1. INTRODUCTION

Recently the theory of the optical absorption has been developed for TCNQ dimer charged negatively by one or two unpaired electrons [1, 2]. These theories appear to be well-suited for TCNQ salts, in which the strongest contribution to the optical absorption can be ascribed to quasi-isolated TCNQ dimers that are present in the crystal structure. Besides these special cases there is a large class of TCNQ salts in which the validity of the dimer approximation is not obvious [3]. Usually the conductive salts contain infinite stacks of TCNQ molecules with the unpaired electrons distributed along the stacks in some way.

One of the simplest charge distributions is perhaps that of TCNQ chains with one electron per molecule. This so-called half-filled band case is represented in nature by the crystal of NaTCNQ [4] at temperatures above 348 K. Another simplifying feature of this salt is the mutual equivalence of molecules of a given chain in which they are stacked with equal interplanar spacings and space orientation. We shall limit ourselves to salts with these two properties in this paper.

It has been widely accepted [5—7] that the Hubbard Hamiltonian [8] expresses very plausibly the correlation interaction in some TCNQ salts. The optical absorption of TCNQ stack with the above-given special structure and the electronic interaction described by Hubbard Hamiltonian was treated by several authors. The single-electron Green's function obtained with the help of Hubbard's decoupling [8] was used in calculation of the real part of the optical conductivity $\sigma_1(E)$ for the optical transitions across the Hubbard gap [9]. In this approximation the correlation of the electronic spin orientations on neighbouring sites was completely neglected. The use of an unrestricted Hartree-Fock method for obtaining the single-electron energy spectrum of the Hubbard Hamiltonian gives another result for $\sigma_1(E)$ [10], which however does not differ qualitatively from that of ref. [9]. Both these approa-
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aches do not offer an easy extension to account for that part of the temperature dependence of $\sigma_z(E)$ that is controlled by the temperature dependence of the ordering of the electronic spins. In addition to that, these two theoretical approaches cannot be easily extended to the case when the original two-parameters Hubbard Hamiltonian is extended by adding the electronic repulsion interaction terms of electrons placed on neighbouring molecules. From the point of view of taking into account the influence of spin correlations somewhat more advanced is the theory of ref. [11] although this formulation was not extended by the authors to the case when the spin ordering is determined by the thermal equilibrium in the system of interacting spins.

The infrared spectra of TCNQ salts display remarkable temperature dependences [12–16]. Because of lack of full understanding of these dependences a theory of the optical properties is needed which allows one to distinguish which part of the temperature dependence is due to thermal variations of the spin correlations. From a more general point of view, it is desirable and also quite natural to build the theory in such a way that the strong electrostatic interaction of electrons including interaction of electrons placed on neighbouring molecules is treated as a zero order Hamiltonian and the remaining interactions including the intermolecular electronic transfer operator as a small perturbation. In order to fulfill such a program this paper uses as its main method the well-known perturbation theory of degenerate states and the technique of effective Hamiltonians.

2. HAMILTONIAN AND THE CURRENT OPERATOR

In the TCNQ salts, which can be considered a collection of more or less noninteracting dimers of TCNQ anions, $2 \text{TCNQ}^2-$, we can work with the two-sites Hubbard Hamiltonian [8] containing only two parameters, the intermolecular transfer integral, $t$, and the on-site coulombic repulsion $I$. However, in other TCNQ salts in which the dimer approximation is not good enough, we generally deal with infinite stacks of the molecules. In these materials we should rather start with the extended Hubbard Hamiltonian [17],

$$H = t \sum_{i} \sum_{\sigma} (c_{i\sigma}^+ c_{i+1\sigma} + c_{i+1\sigma}^+ c_{i\sigma}) + \frac{1}{2} I \sum_{i} \sum_{\sigma} n_{i\sigma} n_{i,-\sigma} + \sum_{\delta \geq 1} V_{\delta} \sum_{i} \sum_{\sigma_1 \sigma_2} n_{i\sigma_1} n_{i+\delta,\sigma_2},$$

$n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$ where $c_{i\sigma}$ is the annihilation operator of an unpaired electron on the site $i$ and with spin $\sigma$. The sum over $i$ covers all $N$ molecular lattice sites in a single molecular stack. An assumption of $N$ being very large allows us to ignore the effects connected with the ends of the stacks. Estimates of magnitudes of all parameters of (1) are available (see for example [17, 18]). In the present work it is assumed that $V_{\delta} = 0$ for $\delta \geq 2$.

The real part $\sigma_z(E)$ of the $z,z$-component of the complex conductivity, with the $z$-axis identical with the axis of molecular stacks, will be calculated in a later section. This quantity can be obtained from the thermodynamic Green’s function [19, 20].