

Dynamic localization in two low-dimensional synthetic semiconductors

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DYNAMIC LOCALIZATION IN TWO LOW-DIMENSIONAL SYNTHETIC SEMICONDUCTORS

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ABSTRACT

The anomalous temperature dependence of the electrical conductivity ($\ln(\sigma) \propto T^{-1/2}$) of the low-dimensional synthetic semiconductors $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ is shown to be a consequence of the thermal vibration of the anions which makes the systems dynamically disordered. For the Ni-compound, the conduction is determined primarily by the number of available carriers. The Pd-compound is a dynamically disordered metal in which the conductivity is determined by the carrier mobility. In both cases the anomalous temperature dependence of the conduction is a consequence of the temperature dependence of the vibrational amplitude of the anions.

INTRODUCTION

This paper offers an explanation for the unusual temperature dependence of the conductivity in the synthetic materials $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ [1]. They belong to the class of compounds $(\text{R}_4\text{N})_x[\text{M}(\text{dmit})_2]$, where M is a transition metal (Ni, Pd, Pt) and R is an alkyl group and $\text{M}(\text{dmit})_2$ is transition metal bis(1,3-dithiole-2-thione-4,5-dithiolato). The $\text{M}(\text{dmit})_2$ group is shown in figure 1. For the two compounds the logarithm of the conductivity scales with $T^{-1/2}$ (see figure 2) rather than with T^{-1} as is commonly found in semiconductors. Just as the latter temperature dependence characterizes the semiconducting state, the $T^{-1/2}$ dependence is the hallmark of hopping conduction between localized states in disordered systems [2,3]. The above mentioned compounds however are statically ordered systems and at first glance there does not seem to be a connection to the standard explanation for the $T^{-1/2}$ -law. We will see below that the systems are effectively disordered, due to the large thermal vibrations of the anions: the transfer integrals are randomly disordered to such an extent that electron localization occurs.

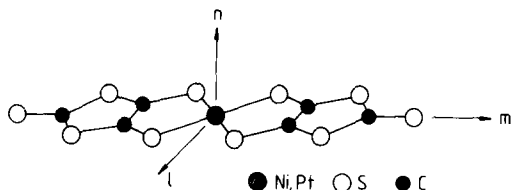
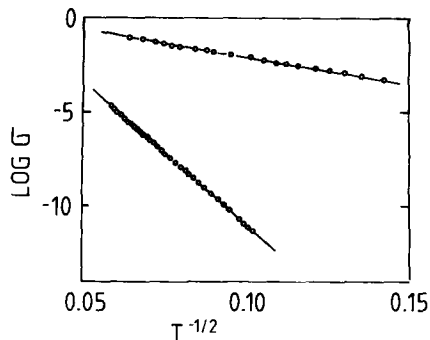


Fig. 1. The $M(dmit)_2$ group and the axes of molecular symmetry.

Fig. 2. Conductivity of $(Et_4N)[Ni(dmit)_2]$ (lower curve) and $(Et_4N)_{0.5}[Pd(dmit)_2]$ (upper curve) plotted vs. $T^{-1/2}$



In a recent paper [4], we have calculated the transfer integrals of a series of compounds within the $(R_4N)_x[M(dmit)_2]$ class. It was found that these calculations give a fair prediction for the band gap, assuming that the Hubbard Coulomb repulsion (U) is larger than the band width ($U = 1.0$ eV, $W \approx 0.5$ eV). Within this series of compounds $(Et_4N)[Ni(dmit)_2]$ and $(Et_4N)_{0.5}[Pd(dmit)_2]$ are peculiar in that respect that there is an order of magnitude difference between different transfer integrals. $(Et_4N)[Ni(dmit)_2]$ is a linear chain compound: the *intrachain* transfer integrals t^{1D} are 0.13 and 0.12 eV respectively, 20 times larger than the largest *interchain* transfer integral t^{3D} , which equals 0.007 eV. $(Et_4N)_{0.5}[Pd(dmit)_2]$ has a planar arrangement of $Pd(dmit)_2$ dimers. The *intradimer* transfer integral (D) equals 0.63 eV; *intraplane* transfer integrals are 0.025 eV, while the *interplane* coupling has a strength of only 0.003 eV. As a consequence of the large *intradimer* matrix element, the dimer splitting ($2D = 1.26$ eV) is the largest parameter of the electronic system and even exceeds the on-site Coulomb repulsion U . This implies that in this system, with one electron per dimer, only the bonding dimer orbital will be occupied, and the system may be considered as a charge transfer salt with 1:1 donor to acceptor ratio and $[Pd(dmit)_2]_2$ as the basic building block. The on-site Coulomb repulsion is now reduced with respect to that of a single $M(dmit)_2$ molecule. A simple calculation predicts $U^* = 0.4$ eV [5]. For reasons explained below, this large difference between different matrix elements is essential for the localization of electrons in these materials.

Table 1

Transfer integrals and their derivatives with respect to molecular displacement

compound	t (eV)	$(1/t) \cdot (\partial t / \partial u_i) (\text{\AA}^{-1})$		
		l	m	n
$(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$	$t_1^{1D} = 1.3 \cdot 10^{-1}$	-0.4	-0.2	-2.2
	$t_2^{1D} = -1.2 \cdot 10^{-1}$	1.0	0.7	1.7
	$t^{3D} = -7.3 \cdot 10^{-3}$	-2.2	-0.5	0.1
$(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$	$D = -6.3 \cdot 10^{-1}$	-0.1	0.4	1.8
	$t_1^{2D} = -2.6 \cdot 10^{-2}$	2.2	-1.8	0.5
	$t_2^{2D} = -2.2 \cdot 10^{-2}$	5.5	0.5	2.4

THE EFFECTS OF ANION VIBRATION

In order to investigate the effect of disorder introduced by anion vibration, we have calculated the derivatives of the transfer integrals with respect to displacement along the axes of molecular symmetry (denoted by l, m and n, see fig. 1). The results for $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ are collected in table 1. The typical value for the relative change in the transfer integral upon displacement is 2\AA^{-1} . The anisotropic thermal parameters indicate that the average vibrational amplitude at room temperature is roughly 0.2\AA , more or less independent of both direction and atom [6]. The above leads to the conclusion that the relative spread in the transfer integrals due to the thermal anion vibration amounts to 40% ! Clearly, the effect of this is not negligible and has to be incorporated in the calculation of the density of states (DOS) of the system. This can be done by considering a finite, randomly disordered lattice. The disordered lattice in our calculation is static and exists only on a timescale that is shorter than the inverse phonon frequency, i.e. 10^{-12} s. This does not pose a problem since the electrons adjust themselves to the lattice on a much shorter time scale, namely $\hbar/W \approx 10^{-15}$ s (W is the band width). In other words: the use of the Born-Oppenheimer approximation is justified. For this statically disordered system we have calculated the energy eigenvalues and eigenfunctions. Figure 3 shows the resulting DOS for both systems as compared to the DOS of the periodic lattice. As expected, the effect of thermal disorder is large. For $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ the gap is filled with a tail that diminishes exponentially as one approaches the Fermi-level. For $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ the effect is even more pronounced because the *intradimer* transfer integral is so large. In this case the system has a finite DOS at the Fermi-level.

Apart from the effect on the density of states, the disorder causes localization of the electron wave function. The inserts of figure 3 show typical eigen functions for the two compounds. One might have anticipated localization on the basis of Anderson's criterion for localization which states that localization should occur if the spread in local energies exceeds $2W$, where W is the band width [7]. For $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$, the relevant bandwidth is

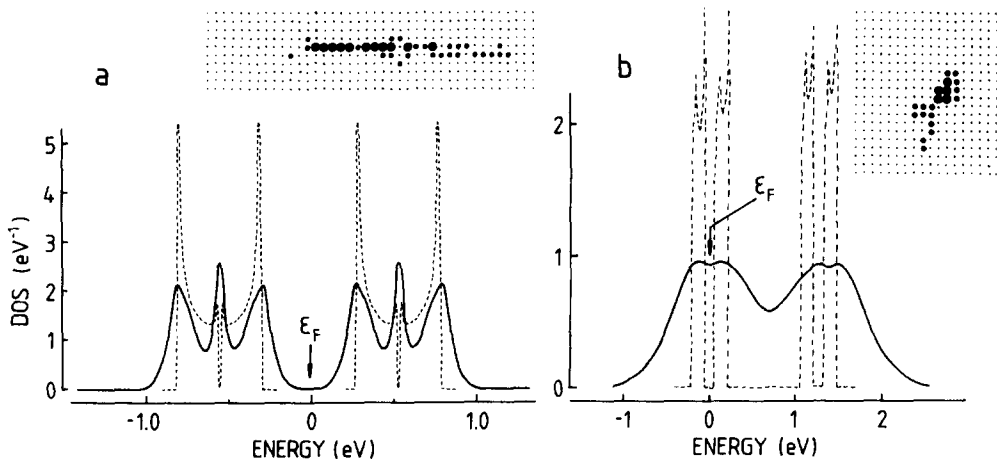


Fig. 3. The electron density of states (DOS) for a static lattice (dashed lines) and a thermally disordered lattice at 300 K (full curves) for $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ (a) and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ (b). The insert shows typical electron eigen functions of the disordered lattice.

the bandwidth of the bonding dimer orbital: 0.17 eV. The energy of this orbital is -0.63 eV, but the uncertainty due to the *intradimer* vibrations is $\pm 40\%$ or 0.5 eV, larger than $2W$. For $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$, the argument is more subtle. In this case localization occurs as a consequence of the low dimensionality of the system. In a truly one-dimensional system any amount of disorder produces localization. A weak *interchain* coupling introduces a threshold for localization: the disorder should exceed $(t^{1D} \cdot t^{3D})^{1/2}$ [8]. This condition is fulfilled. In conclusion, the effect of anion motion on both the DOS and on the character of the electron eigenfunctions is appreciable. Below we will calculate the effect of anion motion on the conduction of these compounds. We will treat both compounds separately because one has a semiconductor-like DOS, while the other resembles a disordered metal.

$(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$: A DISORDERED SEMICONDUCTOR

The effect of thermal disorder in this case is to create an exponential tail of states in the gap region of the rigid lattice. The width of this tail is indicated by $W_{\frac{1}{2}}$. One expects these states to be important in determining the conductivity since they are closest to the Fermi-level. This effect can be calculated using the relation

$$\sigma = 2 \cdot e \cdot \mu \cdot \int_{-\infty}^0 d\epsilon n(\epsilon)(1 - f(\epsilon)) \quad (1)$$

The factor 2 stems from the fact that the DOS is symmetrical with respect to ϵ_F . We have assumed that the DOS is constant for energies farther than E_a from the Fermi-level and that below this energy an exponential tail fills the gap with a half-width $W_{\frac{1}{2}}$. The integral over the DOS gives then two contributions to the conductivity:

$$\sigma = \sigma_T \cdot e^{-E_a/W} \frac{1}{2} + \sigma_B \cdot e^{-E_a/kT} \quad (2)$$

The second term is the normal semiconductor contribution; the first term is new and results from the band tail. The temperature dependence of this term comes from $W \frac{1}{2}$. The broadening of the band is proportional to the vibrational amplitude of the anions, which itself is proportional to the square root of temperature. Hence, the leading term at low temperatures is the first one, which has the anomalous $T^{-1/2}$ dependence that is observed in this compound. Furthermore, the values for both E_a (0.25 eV) and $W \frac{1}{2}$ (0.020 eV at room temperature) as obtained from our calculation are in perfect agreement with the experimental values.

(Et₄N)_{0.5}[Pd(dmit)₂]: A DISORDERED METAL

The effect of thermal anion vibration on the electron DOS is even more pronounced in the case of (Et₄N)_{0.5}[Pd(dmit)₂], where the dynamical spread of the largest electronic parameter (the dimer splitting) causes a finite DOS at the Fermi-level. This implies that the system should be considered to be a disordered metal, similar to e.g. Quin-TCNQ₂ or KCP [2,9]. In these compounds, the disordered is static and stems from the disorder of the donor system which produces a random potential on the conducting chain. As shown by Bloch, Weisman and Varma[2], a whole class of these compounds exists that invariably exhibit the $T^{-1/2}$ -law for the conductivity. Such a broken-power law is theoretically explained in terms of hopping between localized states over a variable distance (variable range hopping, VRH) [3]. Depending on the details of the model one finds that the $\ln(\sigma)$ scales with T^α with $\frac{1}{4} < \alpha < \frac{1}{2}$.

In the case we consider here, the localization is dynamic in origin and the localized wave functions change on the phonon time scale, i.e. 10^{-12} s. Moreover, the source of localization, i.e. the amplitude of the lattice vibrations is temperature dependent. This implies that some modifications have to be made in the theory. The conductivity of a disordered metal is determined by the carrier mobility, which in turn is proportional to the hopping probability (Γ) between localized states:

$$\Gamma = \nu_0 \exp(-\alpha R - \Delta/kT) \quad (3)$$

where ν_0 is a constant of the order of the phonon frequency; α denotes the decay rate of the localized wave function and Δ is the energy difference between the two localized states under consideration, separated by a distance R . In the standard VRH theory the hopping distance is such that the hopping probability is maximal. If one considers hopping over large distances, the mean energy separation between states will be smaller and therefore the hop is thermally facilitated. On the other hand the overlap is smaller, which depresses the hopping probability. The optimal hopping radius is determined by the balancing of these two effects. The outcome is that the hopping distance increases as the temperature is lowered. In the case of dynamic localization, the hopping distance cannot increase beyond a certain point [10]: since the localized wave function is constructed via constructive interference of the electron with itself, and in this case only a limited time is available, there has to be a

certain cut-off in the radius of the wave function. Our calculations indicate that the cut-off radius is smaller than the hopping radius would have been if we had applied the standard argument of the VRH theory. In the modified theory, the hopping probability is determined by the temperature dependence of the cut-off radius, which varies with temperature as a consequence of the temperature dependence of the anion vibrational amplitude. The cut-off radius determines both the typical overlap between neighbouring wave functions, which enters into the first term of the exponent of equation 3 as well as the typical energy separation between states that enters via the second term. Numerical calculations indicate that in the case of $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$, the log of the conductivity scales with $T^{-1/2}$ as a direct consequence of the $T^{1/2}$ dependence of the vibrational amplitude of the anions.

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