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PEIERLS GAP IN THE LARGE-*U* QUARTER-FILLED BAND COMPOUND QUINOLINIUM TETRACYANOQUINODIMETHANIDE [Qn(TCNQ)$_2$]

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Abstract

We report here the first measurements showing directly the existence of a Peierls gap, $2\Delta_P$, on the TCNQ chains of Qn(TCNQ)$_2$, a quarter-filled band quasi-one-dimensional conductor with strong on-site electron–electron correlations ('large U') and disorder on the cation chains. The temperature dependence, $\Delta_P(T)$, obtained from the T-dependence of the a_g mode absorption of TCNQ, shows that the gap decays slowly; we believe this effect is due to a small additional potential on the TCNQ chains with the Peierls periodicity.

Qn(TCNQ)$_2$ is a quasi-one-dimensional crystal with quarter-filled conduction band and room temperature conductivity ~100 ohm^{-1} cm^{-1} due to electrons on the TCNQ chains [1]. On cooling, its conductivity σ is found to increase slightly, reaching a plateau in the range 200 - 240 K, beyond which it decreases rapidly with further decrease in T [1]. Similar behavior is observed for (NMP)$_x$(Phen)$_{1-x}$(TCNQ) with $x \simeq 0.5$, which also has a quarter-filled conduction band and large U. Both compounds have cation chain disorder, consisting of a random arrangement of the dipoles on the Qn molecules in the one case [2] and randomness in the arrangement of excess NMPs for $x > 0.5$ in the other. On the basis of the theorem that all electronic states in a disordered one-dimensional structure

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are localized, many workers have presented explanations of the T-variation of σ and other properties of $Qn(TCNQ)_2$ based on the electrons on the TCNQ chains being localized due to the disorder on the other chains [3 - 5]. Another type of disorder model, random barriers localizing the electrons on the TCNQ chains, has also been used to account for some properties of $Qn(TCNQ)_2$ [6]. By contrast Epstein *et al.* proposed that the electrons on the TCNQ chains are not localized. They postulated the existence of a gap at the Fermi energy and band carriers with sizeable mobility to account for σ and its variation with T [1, 7]. We have now obtained optical absorption data for these materials that show they have gaps to the highest T measured, 300 K. Further, the symmetric (a_g) lattice modes of TCNQ are strongly represented in the absorption spectrum, indicating that the gaps, in large part at least, are due to Peierls distortion [8 - 11]. From the variation of the a_g mode absorption amplitude with T we deduce that the Peierls gap decays slowly rather than abruptly, as expected in mean field theory. We believe this behavior is due to an additional potential V_0 on the TCNQ chains with the periodicity of the Peierls distortion, $4k_F$ due to the large U. V_0 could be due to the cation chains themselves providing a small Fourier component of potential at $4k_F$ or to Coulomb repulsion.

A unique feature of $(NMP)_x(Phen)_{1-x}(TCNQ)$ is the fact that for $0.5 \leqslant x \leqslant 0.56$, electrons in excess of 0.5/lattice site go into soliton states in the gap [12 - 14]. Because $Qn(TCNQ)_2$ is very similar in structure and properties to $(NMP)_x(Phen)_{1-x}(TCNQ)$ for $x \simeq 0.5$, we speculate that $Qn(TCNQ)_2$ samples also have solitons. This includes thermally generated ones and probably some due to accidentally incorporated impurities. We have calculated the temperature dependence of the gap in $Qn(TCNQ)_2$ incorporating solitons as well as V_0 and find reasonable agreement with the experimental results for $V_0 \sim 25$ K.

Because the crystals were too small for reflectance studies, absorption measurements were made on composite samples prepared by grinding and mixing many small crystals with an insulating host and compressing the mixture into a pellet. The typical crystal size in these samples was several microns and the volume fraction in the mixture was below 0.01. Thus the crystals were isolated in the host; the absorption coefficient of the TCNQ salts could be determined after correcting for the absorption and reflection of the host. In the frequency range studied (below 4000 cm^{-1}) this absorption is mostly from the TCNQ chain direction. Measurements were made in two overlapping frequency regions. From 50 to 800 cm^{-1} a homebuilt Michelson interferometer was used to study paraffin-host samples. Low-temperature measurements were made by putting the samples in the detector cryostat. Between 600 and 4000 cm^{-1} a Digilab rapid-scanning interferometer was used to study KCl-host specimens. Use of a Helitran continuous-flow refrigerator enabled the low-temperature measurements to be made.

Absorption coefficients *versus* frequency for $Qn(TCNQ)_2$ at 6, 100, 200 and 300 K is shown in Fig. 1. The nine structures indicated by arrows

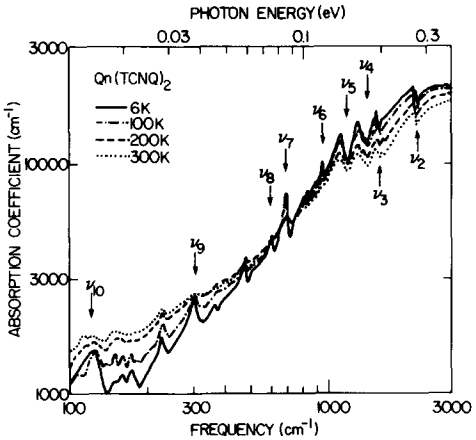

Fig. 1. Absorption coefficient *vs.* frequency for $Qn(TCNQ)_2$ at 6, 100, 200 and 300 K. The arrows indicate the a_g modes. Note the logarithmic scales.

are very close in psotion to nine out of 10 a_g totally symmetric modes [15] of $TCNQ^-$. These modes, expected to be infrared inactive because they are totally symmetric, appear strongly in infrared absorption in $(TEA)(TCNQ)_2$ [8], (TTF)(TCNQ) [9], $(TTF)Br_{0.76}$ [10] etc. Their appearance in these cases has been shown to be due to the presence of phase oscillations of a charge density wave, the theory [11] based on this effect being in good agreement with the observed absorption [8 - 10]. Although disorder could, by destroying symmetry, cause some modes to become i.r. active, this should be a small effect for the a_g modes so long as the molecules retain their shape. It should be noted that in $TEA(TCNQ)_2$ there is also orientational disorder on the TEA chains [16]. We conclude that the observation of strong a_g absorptions is evidence that the observed gap in $Qn(TCNQ)_2$ is largely a Peierls gap.

The variation of σ with T can be fitted with a gap value of 1200 K for $Qn(TCNQ)_2$ [1]. Although, as seen in Fig. 1, the absence of absorption below $\sim$100 cm^{-1} indicates that there is a gap, there is no well-defined absorption edge to identify that gap. The onset of absorption at frequencies well below the gap and the continuous increase of absorption with frequency to well past the band edge obtained from σ *versus* T are also seen in (TTF)-(TCNQ) and other TCNQ compounds [17]. The origin of the absorption is unknown; it may be partly due to solitons [17]. It is possible to obtain an approximate value for the total gap, 2Δ, from observation of the a_g modes. For frequencies below $2\Delta/\hbar$ they should appear as ordinary resonances or peaks, whereas above this frequency they should be Fano-type anti-resonances in which there is an absorption minimum at the mode frequency, preceded by a maximum on the low-frequency side [18]. We judge from this crossover that at 6 K the gap is between 700 and 950 cm^{-1} [19]. These frequencies neatly bracket the gap found [1] by fitting σ *versus* T, 1200 K or 840 cm^{-1}.

At 300 K the resonances and anti-resonances due to the a_g modes are seen in Fig. 1 to be much less pronounced. The T-dependence is shown quantitatively in Fig. 2 where we plot the oscillator strength for the modes ν_7 - ν_{10}, normalized to their 6 K values, against T. Qualitatively similar results are obtained for the modes higher in frequency than ν_7 but are not shown because it is more difficult to determine oscillator strength for the Fano lineshape. Because the a_g modes appear only due to the Peierls distortion, within mean-field theory the data of Fig. 2 should represent the T-variation of the Peierls gap $2\Delta_P$ normalized to its low temperature value $2\Delta_P(0)$ [9, 10, 17]. The slow decrease of the gap with T above ~150 K is, however, not characteristic of the Peierls gap in mean field theory. One might speculate that Δ_P actually goes to zero at ~150 K and the slow decrease in the oscillator strength thereafter is due to fluctuations interacting with the molecular vibrations, as is reported for the TTF chain in TTF–TCNQ [9]. However, as indicated earlier, σ is still increasing with T from 150 to 200 K, and has a plateau from 200 to 250 K, indicating that there still is a gap in at least that temperature range. Above 250 K the rate of decrease of σ with T is much smaller than the T^{-2} that is typical for the metals in this family of materials. This indicates that carrier concentration is still increasing with T above 250 K, *i.e.*, the gap is still present [1].

We suggest that the persistence of the gap is due to the presence of a periodic potential V_0 on the TCNQ chains. As will be discussed below, the presence of solitons is also necessary to account for the T-dependence of the gap. The potential V_0 must have the same periodicity as the Peierls distortion and could be due to neighbouring chains or to intrachain Coulomb repulsion [20, 21]. As regards the former, the Qn chains do not have charge alternation but the random arrangement of dipoles on the Qn chain will result in a small Fourier component of electrostatic potential on TCNQ with the periodicity of the Peierls distortion. The Coulomb

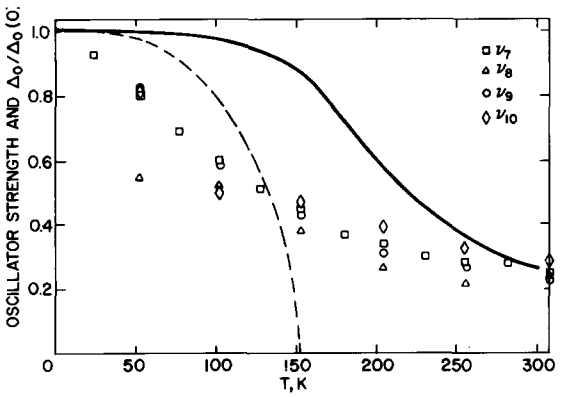

Fig. 2. The data points represent oscillator strength (normalized to the 6 K value) *vs.* temperature for the TCNQ a_g modes ν_7 (691 cm^{-1}), ν_8 (600 cm^{-1}), ν_9 (306 cm^{-1}) and ν_{10} (124 cm^{-1}) in $Qn(TCNQ)_2$. The lines represent the calculated temperature dependence of $\Delta_P/\Delta_P(0)$ accounting for solitons; the dashed curve assumes a zero external potential, the solid curve assumes a V_0 of 25 K.

contribution to V_0, for the quarter-filled band case, would come from $V_1 - 2V_2$, V_1 and V_2 being nearest neighbor and next nearest neighbor repulsions [20]. Only a small value of V_0 is required to produce the behavior shown in Fig. 2, as may be seen from the following argument. What destabilizes the Peierls transition is the excitation of electrons from valence band to conduction band with increasing T. This excitation is prevented by the total gap, $2\Delta = 2(\Delta_P + V_0)$. The fact that Δ_P decays about as expected (or more) for a purely Peierls gap up to ~100 K, as seen in Fig. 2, indicates that $V_0 \ll \Delta_P(0)$. Thus $\Delta_P(0) \simeq 600$ K, as obtained [1] from σ *versus* T, and more or less in agreement with the value deduced from optical absorption. This would make $\Delta_P(300\ \text{K}) \simeq 150$ K, according to Fig. 2. The fact that Δ_P is still decaying at room temperature means $V_0 < 150$ K. This places an upper limit on the gap due to Coulomb repulsion that is considerably smaller than expected [20]. The difference is probably due to the extremely large dielectric screening parallel to the chains in $Qn(TCNQ)_2$ [6].

In principle one could, neglecting solitons, find V_0 by fitting $\Delta_P/\Delta_P(0)$ *versus* T of Fig. 2 using the gap equation obtained by minimizing the free energy of lattice and electrons with respect to the full gap 2Δ [22, 23]. Only two parameters may be specified: $2\Delta(0)$, which we take, from σ, to be 1200 K, and the bandwidth, which we take as 4500 K, because the TCNQ spacing is somewhat larger than that in TTF–TCNQ where the bandwidth is ~6000 K. Having specified these, we find from the gap equation that, even for $V_0 = 0$, $\Delta_P/\Delta_P(0) = 0.57$ at 300 K, the gap disappearing only at 700 K. Thus no value of V_0 will allow a fit to $\Delta_P/\Delta_P(0)$, because $V_0 = 0$ can only slow the decay of the gap. The prediction of too high a transition temperature for a given $\Delta(0)$ is a familiar problem for Peierls theory [24]. Agreement of experiment with theory is improved if the existence of solitons is allowed for, because the extra carriers to which they give rise decrease the transition temperature [14].

Because the gap in these materials is predominantly a Peierls gap, we expect the occurrence of pairs of thermal solitons [25] whose creation energy is $2\Delta/\pi$ [25]. If there are small deviations from the quarter-filled band, the excess electrons or holes should be housed in soliton states [25], as has been found for $(NMP)_x(Phen)_{1-x}(TCNQ)$ for $0.50 \leqslant x \lesssim 0.56$ [12]. For $Qn(TCNQ)_2$ samples the temperature variations of σ and thermopower resemble those of $(NMP)_x(Phen)_{1-x}(TCNQ)$ samples for $x \simeq 0.54$, *i.e.*, ~4% donors [26]. This concentration is also consistent with X-ray measurements of the low-temperature correlation length along the chain of 40 Å or ~10 lattice sites [27], when the length of a soliton is taken into account. In any case, we have calculated $\Delta_P/\Delta_P(0)$ of $Qn(TCNQ)_2$ for donor concentrations of 0, 2 and 4%, the former representing thermal solitons only. The gap equation for this case is obtained from that in ref. 14 by replacing Δ with $\Delta_P + V_0$ in all terms but that for the lattice deformation. Inclusion of solitons allows a reasonable fit to experimental data. We find that the ratio $\Delta_P/\Delta_P(0)$ is fairly insensitive to chemically induced soliton concentration.

The fit shown in Fig. 2 is for $V_0 = 25$ K, but about as good fits are found for V_0 in the range 20 - 30 K. Agreement with experiment would be enhanced if allowance were made for the spread of soliton levels in the gap.

In conclusion, we have shown that in the quasi-one-dimensional compound $Qn(TCNQ)_2$ disorder on neighboring chains does not localize electrons on the TCNQ chains. Infrared absorption data establish the existence of a Peierls gap to room temperature, and presumably beyond. The slow decay of the Peierls gap is evidence for an additional potential V_0 on the chains with the Peierls periodicity $4k_F$. V_0 could be due to Coulomb effects or to a Fourier component of the random potential on the anion chains. The observed decay of the Peierls gap with T for $Qn(TCNQ)_2$ can be fitted if the existence of solitons is taken into account; it leads to $V_0 \simeq 25$ K.

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