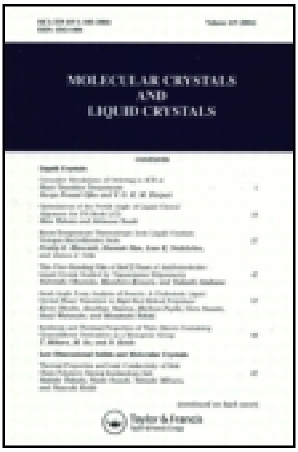

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Experimental Evidence for the Role of Zero-Point Motion in a One-Dimensional Material: Optical Studies of an MX Solid

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EXPERIMENTAL EVIDENCE FOR THE ROLE OF ZERO-POINT MOTION IN A ONE-DIMENSIONAL MATERIAL:OPTICAL STUDIES OF AN MX SOLID

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ABSTRACT Luminescence and resonance Raman spectra have been measured for the quasi-one-dimensional charge-density-wave material [Pt(en)$_2$][Pt(en)$_2$Cl$_2$](ClO$_4$)$_4$; en=1, 2-diaminoethane, PtCl. While the luminescence experiments show the existence of tail states at low temperature in the band gap region, the Raman measurements conclusively demonstrate that this tail does not arise from ordinary static structural disorder. These results can be explained by considering the zero-point motion of the lattice.

INTRODUCTION

It has been known for some time that the zero-point motion in *trans*--polyacetylene (PA) is comparable to the Peierls distortion.[1] In a recent paper, this was pointed out to be true for a wide range of one-dimensional (1-D) solids.[2] Under certain approximations, zero-point and thermal lattice motion can be treated as a static random potential that removes the inverse square-root singularity in the density of states at the gap energy and produces a finite density of electronic states within the gap. Experimentally, this is be manifested as a temperature-dependent optical absorption tail extending into the gap region, with a zero-point contribution observable even as T goes to zero. Such effects have also been qualitatively predicted by others using semiclassical Monte Carlo techniques.[3] While band tail absorption is observed in PA [4] and other 1-D materials, it is generally difficult to definitively rule out static disorder (i. e. ordinary inhomogeneous broadening) as an origin for the tail states.

The luminescence excitation spectra for a crystal of PtCl broadens significantly as the temperature is increased, Figure 1.[5] Furthermore, even at low temperatures, a tail is observed in the excitation profile for energies lower than approximately 2.36 eV or 525 nm. Direct absorption measurements in the band tail region show a similar temperature dependence.[6] It is reasonable to conclude that the band edge is smeared out by some kind of disorder.

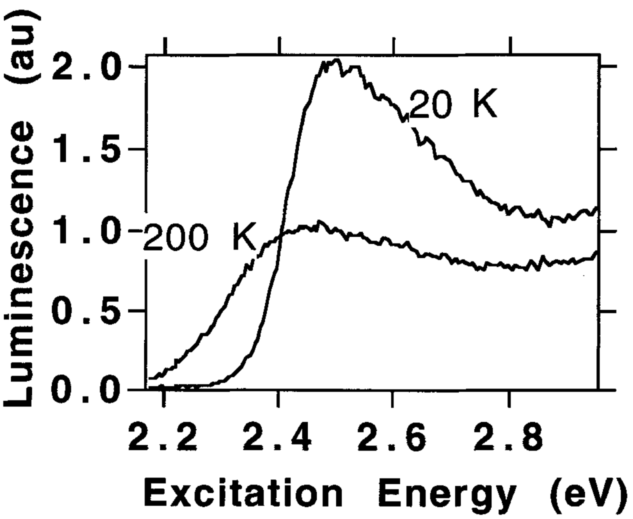

Figure 1: Excitation Spectra at 20 K and 200 K for PtCl.

To determine to what extent structural inhomogeneities could be present in our crystals, we have performed RR measurements with excitation energies throughout the band gap and band tail region, from 1.96 eV to 2.71 eV, carefully monitoring the symmetric Cl stretch frequency,

ν_1, frequency as a function of excitation energy. A monotonic correlation between ν_1 and the band edge is expected for a Peierls distorted system.[7] From the ligand and counterion substitution studies, we find that ν_1 shifts by 38 cm^{-1} per eV shift of the the band edge.[8] Therefore any kind of static structural disorder (strains, vacancies, interstials, etc.) coupled to the CDW and electronic gap would be manifested also by shifts in the ν_1 frequency as the Raman excitation comes into resonance with various local environments as it is tuned through the band edge region. For example, a ν_1 shift of 2.5 cm^{-1} is expected between excitations of 2.41eV and 2.34 eV (two convenient Ar^+ laser lines in the tail region), greater than the observed width of the n_1 band in $Pt^{35}Cl$, an effect which would be easily seen within our experimental uncertainty of 0.3 cm^{-1}.

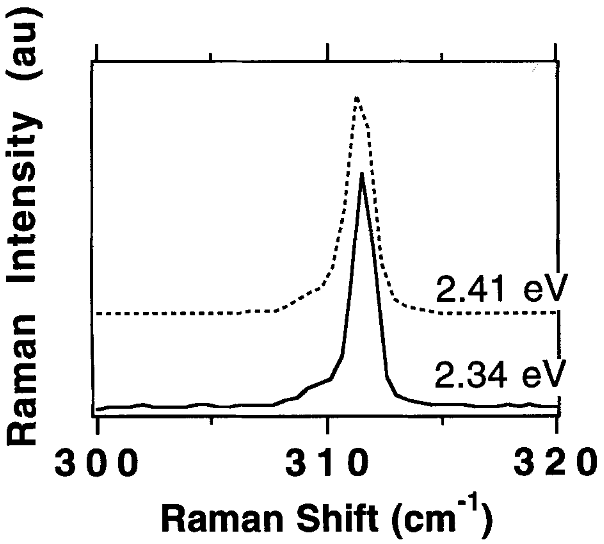

Figure 2: Excitation dependence of the ν_1 Raman spectrum at 20 K for PtCl made with isotopically pure ^{35}Cl.

With inhomogeneous broadening thus ruled out, lattice fluctuations are a likely origin of the tail states seen in our luminescence experiments. Because of the lack of structural disorder, MX solids provide a good testing ground for the theory of reference 2. They predict that as the temperature is increased the density of states in the gap will increase and will produce a large broadening in the absorption band edge. This is totally consistent with what we see experimentally. Furthermore, it is noted in reference 2 that these band tail states should be localized. The tail width of the density of states is equal to $\Delta \eta^{2/3}$, where η is given by

$$\begin{aligned} \eta &= \eta_0 \coth\left(\frac{\hbar\omega}{2k_BT}\right) \\ \eta_0 &= \lambda \frac{\pi \hbar \omega}{2\Delta} \end{aligned} \qquad (1)$$

and 2Δ is the Peierls energy gap, ω is the phonon frequency, λ is a dimensionless electron-phonon coupling constant defined in Ref. 2. It is important to note that the temperature dependence has also been predicted for exciton-phonon lineshapes in one dimension.[3] From structural and spectroscopic data on PtCl chains with various ligands and counterions, we obtain a nearly linear relation between the gap Δ and the Peierls distortion u_0, with a slope of 2.8 eV/Å; this translates to a value of 0.48 for λ and, letting ω correspond to ν_1=311 cm^{-1}, a value of 0.024 for η_0. Thus, using the experimentally determined value for 2Δ of roughly 20100 cm^{-1} at 20 K, the predicted zero-temperature tail width is then $\Delta\eta_0^{2/3}$=844 cm^{-1}. This is in surprisingly good agreement with the observed 20K tail width of 710 ± 30 cm^{-1}, obtained by fitting the tail region to a Gaussian.[5] A direct comparison of the theoretical density of states to our experimental excitation spectra is given in Fig 3a; unfortunatly, no calculation of the luminescence excitation spectra is available. The temperature dependence, however, indicates that ν_1 is not the only phonon involved, and that much lower energy vibrations contribute strongly to the temperature broadening. By comparing the temperature dependence of the tail width to Eq. (1), an effective phonon frequency of 130 cm^{-1} is obtained.[5] We note that this frequency is in the range predicted for the weakly IR-active Pt-Pt stretch mode.[9]

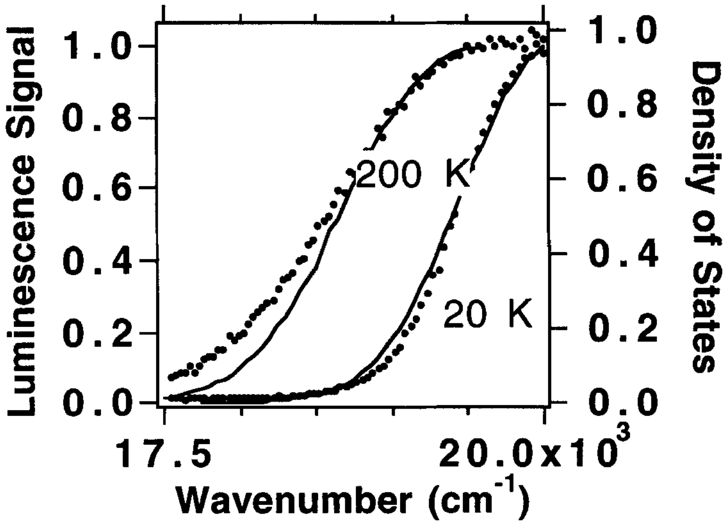

Figure 3. (a) Comparison of the data of Fig. 1 (dots, left scale) to the density of states predicted in Ref 2 for a 311 cm^{-1} phonon, $\eta_0=0.024$ (solid lines, right scale).

The experimental results reported here support the existence of band tail states, reminiscent of the Urbach tail seen in semiconductors, for a 1-D CDW material.[10] Of the 1-D materials studied to date, this class of materials is unique, to the best of our knowledge, in that the resonance Raman experiments rule out structural inhomogeneities as the origin of the band tail states; thus the evidence strongly supports modulation of the Peierls gap by the effective "disorder" originating from zero-point lattice fluctuations as the origin for these tail states, as predicted in reference 2. In contrast, tail states observed in materials like trans-polyacetylene are most likely dominated by contributions from static structural disorder.

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