VOLUME 71, NUMBER 5 PHYSICAL REVIEW LETTERS 2 AUGUST 1993

Evidence for Modification of the Electronic Density of States by Zero-Point Lattice Motion in One Dimension: Luminescence and Resonance Raman Studies of an *MX* Solid

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(Received 27 January 1993)

Luminescence spectra, both emission and excitation, and the excitation dependence of the resonance Raman spectra, have been measured for the quasi-one-dimensional charge-density-wave material $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$, en = 1,2-diaminoethane. 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.

PACS numbers: 71.20.Hk, 72.15.Nj, 78.55.Kz

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 Letter, this was pointed out to be true for a wide range of one-dimensional (1D) solids [2]. Using the Born-Oppenheimer approximation and assuming that the relevant lattice motion can be relegated to a single dispersionless phonon branch, the effect of lattice fluctuations on the electronic density of states for a Peierls-Fröhlich material was predicted. Under these 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 should 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 1D materials, it is generally difficult to definitively rule out static disorder (i.e., ordinary inhomogeneous broadening) as an origin for the tail states. Resonance Raman (RR) studies, for instance, have established the presence of static structural disorder in PA, making inhomogeneous broadening a strong candidate for the origin of the tail states observed in this material [5]. This conclusion is probably true for most organic polymer systems. We present here the results of optical studies on a 1D metal-halogen-mixed-valence (*MX*) solid—$[Pt(L,L)][Pt(L,L)Cl_2](ClO_4)_4$, L = 1,2-diaminoethane (hereafter abbreviated "PtCl") which provide strong support for electronic modulation by zero-point lattice motion: This systematic study demonstrates the existence of a substantial band tail even at the lowest temperatures, while also showing that the samples studied lack static disorder of sufficient magnitude to account for this tail.

The *MX* class of materials are 1D crystalline solids composed of chains of alternating transition metal and halide ions [6]. These systems typically display a commensurate charge density wave (CDW) on the metal ions, accompanied by a Peierls distortion of the halide sublattice, and are of particular interest for the extreme tunability (chemically and structurally) of their *e*-*e* and *e*-phonon couplings and thus CDW strengths. These materials have been successfully modeled using a $\frac{3}{4}$-filled, two-band Peierls-Hubbard Hamiltonian which bears intriguing similarities to those appropriate for other electronically low-dimensional solids including the high-T_c oxide superconductors [7]. For these reasons, these materials have been the subject of extensive experimental and theoretical investigation [7–23].

Particularly important for this work, the strength of the CDW and thus the Peierls distortion, for a given choice of metal and bridging halide (Pt and Cl in this case), can be controlled by the choice of ligands and counterions [9–11]. This control is possible because the three-dimensional hydrogen-bonded network formed by the ligands and counterions forms a template which determines the Pt-Pt spacing along the relatively soft Pt-Cl chain axis [11]. We have employed such structural modifications to establish quantitative empirical relationships among the various observables dependent upon the CDW strength. Most relevant here is the establishment of a relationship between the frequency of the Raman active optic phonon (ν_1) and the optical absorption edge, which allows resonance Raman measurements of ν_1 to be used to determine whether or not the observed band tail absorption arises from static disorder.

The crystals were grown using previously published methods [10]. The luminescence spectra were collected with a SPEX flourimeter outfitted with an IR-sensitive photomultiplier tube (PMT) and gratings blazed for 1000 nm. The data have been corrected for the spectral response of the PMT. Raman measurements were performed using Ti:sapphire, HeNe, and Ar^+ lasers and pre-

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viously described charged coupled device array and PMT detection schemes [18]. To avoid laser heating of the sample, laser power was lowered until no heating effects were observed in Raman spectra.

The luminescence excitation spectra broadens significantly as the temperature is increased; see Fig. 1. 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 [16]. For an ideal, static one-dimensional lattice, one would expect an inverse square-root divergence of the absorption above and no absorption below the band edge. It is reasonable to conclude that the band edge is smeared out by some kind of disorder.

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 to 2.71 eV, carefully monitoring the ν_1 frequency as a function of excitation energy. Since the ν_1 phonon is an oscillation along the Peierls coordinate, drastic enhancement of ν_1 Raman scattering occurs when the exciting photons are in resonance with the gap energy. Furthermore, ν_1 is sensitive to exactly those perturbations which affect the chain's electronic states, and such perturbations shift ν_1 and the band edge in the same direction [16]. This monotonic correlation is expected for a Peierls distorted system [24]. From the ligand and counterion substitution studies, we find that ν_1 shifts by 38 cm^{-1} per eV shift of the band edge. 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 2.41 and 2.34 eV (two convenient Ar$^+$ laser lines in the tail region), greater than the observed width of the ν_1 band in Pt^{35}Cl, an effect which would be easily seen within our experimental uncertainty of 0.3 cm^{-1}. We have performed this experiment on a variety of PtCl samples, at temperatures from 15 to 300 K on two separate spectrometers, both with natural Cl isotopic abundance and with isotopically pure ^{35}Cl and for the best quality crystals, which comprise a majority of our samples, no measurable shift or line shape change was found. We note, however, that several of our samples do display ν_1 shifts on the order of 1 cm^{-1}, in the expected direction, between excitation energies of 2.41 and 2.34 eV; these samples are visibly of lesser quality and typically also display macroscopic nonuniformities as evidenced by shifts in ν_1 as the laser spot is moved to various positions on the sample. Other workers have recently explored the spectroscopic effects of intentional PtCl sample degradation by grinding and polishing, and also observe ν_1 shifts in the damaged samples [21]. Early studies by Kurita and co-workers and Clark and co-workers also show a dependence of the ν_1 frequency on excitation energy, which would be consistent with poor quality crystals with large inhomogeneities [9,17]. Taken together, these results add weight to our argument that structural disorder in PtCl can be sensitively detected by resonance Raman measurements. Figure 2 shows the results of this test performed at 20 K on the same sample used for the luminescence studies, with the sample maintained below 100 K between the two experiments to avoid the structural phase change which PtCl undergoes at 19 °C [20]. The lack of any shift in ν_1 shows that static structural disorder has no significant effect on the electronic or vibrational spectra of this sample. These results are in dramatic contrast to the RR of PA [5].

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

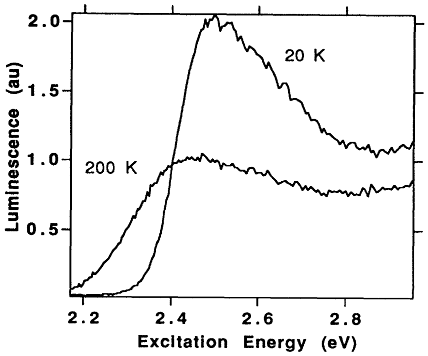

FIG. 1. Excitation spectra at 20 and 200 K for PtCl. Plotted is the intensity at the peak of the 1000 nm luminescence band as a function of excitation energy. A low-energy tail of width $\gg k_B T$ is clearly observed, even at low temperature. As the temperature is raised, this tail broadens significantly.

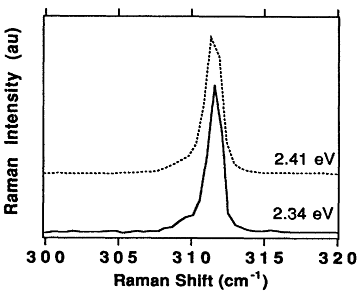

FIG. 2. Excitation dependence of the ν_1 Raman spectrum at 20 K for PtCl made with isotopically pure ^{35}Cl. Excitation energies are noted on the right. Within experimental error, no change is seen in the ν_1 frequency, demonstrating that static disorder of the kind which could modulate chain states is negligible.

ground for the theory of Ref. [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 Ref. [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

$$\eta=\eta_0\coth(\hbar\omega/2k_BT),\quad \eta_0=\lambda\pi\hbar\omega/2\Delta\,, \tag{1}$$

and 2Δ is the Peierls energy gap, ω is the phonon frequency, and 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 line shapes 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 $\nu_1=311$ cm^{-1}, a value of 0.024 for η_0. Thus, using the experimentally determined value for 2Δ of roughly 20 100 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 20 K tail width of 710 ± 30 cm^{-1}, obtained by fitting the tail region with a Gaussian. A direct comparison of the theoretical density of states to our experimental excitation spectra is given in Fig. 3(a); unfortunately, 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), as shown in Fig. 3(b), an effective phonon frequency of 130 cm^{-1} is obtained. We note that this frequency is in the range predicted for the weakly IR-active Pt-Pt stretch mode [23].

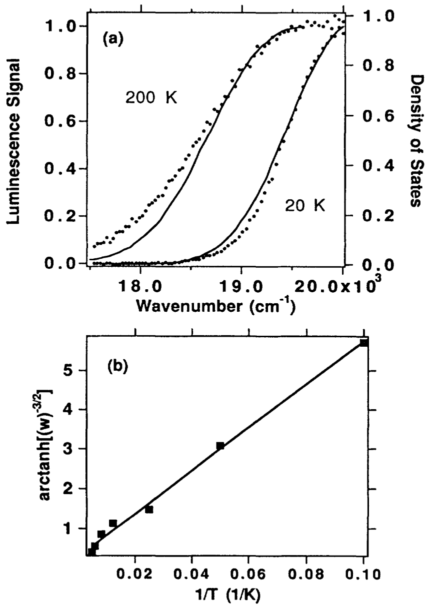

FIG. 3. (a) Comparison of the data of Fig. 1 (dots, left scale) to the density of states predicted in Ref. [2] for a 311 cm^{-1} phonon, $\eta_0=0.024$ (solid lines, right scale). The 200 K spectrum has been rescaled for comparison purposes (see Fig. 1). (b) Experimental temperature dependence of the band tail width, plotted according to Eq. (1); w is the normalized width of the excitation profile tail. An effective phonon frequency of 130 cm^{-1} is extracted from the slope.

This departure of the temperature dependence from the theory of McKenzie and Wilkins is not surprising, since the theory assumes a single dispersionless phonon, while in many 1D systems several different phonons can couple to the Peierls coordinate [5]. At low temperature, the zero-point motion of the phonon most strongly coupled to the electron (ν_1) will dominate, while at higher temperatures, the larger thermal populations of lower energy modes will compensate for their weaker coupling. The excellent agreement between the observed 20 K tail width and that predicted from the theory is actually quite surprising, given that the theory treats only the density of states [2]. Furthermore, the theory is only strictly valid for systems where the bandwidth is larger than the Peierls gap, which is not the case for *MX* solids [7]. Nevertheless, these results strongly support the basic mechanism of electronic modulation by zero-point fluctuations.

The effective disorder caused by zero-point lattice fluctuations is distinguished from ordinary static disorder in that it is seen only by the electronic states. The vibrational transition energies, of course, are still perfectly defined, consistent with the previously discussed Raman spectroscopy. Electronic spectroscopy is sensitive to zero-point motion effects because vertical transitions occur on much faster time scales and are therefore sensitive to modulations of the band gap due to vibrational motion.

The excitation dependence of the luminescence also supports the existence of localized tail states below the band edge. At low temperatures, the luminescence from excitation into the tail of the PtCl band gap is clearly redshifted with respect to luminescence that originates from excitation into the band gap or above; see Fig. 4. At temperatures above 200 K, the excitation energy dependence of the luminescence emission profile disappears (data not shown). At higher temperatures, the excitation dependence disappears because the relaxation rate from the band to the localized tail states increases sufficiently so that all luminescence originates from the lowest lying excited electronic states.

Physically the zero-point lattice fluctuations induce a series of localized electronic states below the band edge. The observed excitation dependence of the luminescence suggests that the photoexcitation dynamics of these sys-

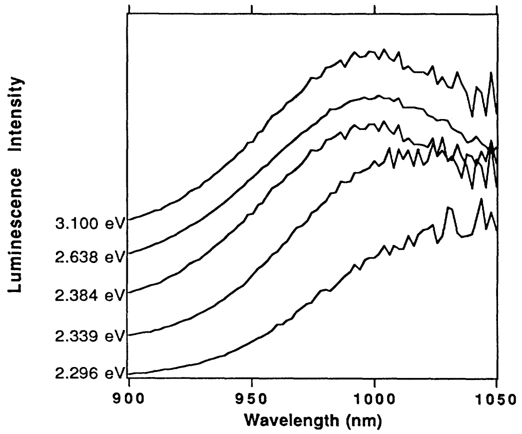

FIG. 4. Excitation dependence of the PtCl luminescence at 20 K for five excitation energies, shown at left. When the band tail states are excited, the luminescence is strongly redshifted.

tems involve nonadiabatic transitions between the band and the localized tail states. Typically theoretical modeling of the photoexcitation dynamics for low-dimensional systems has included only the adiabatic relaxation of the lattice around the initially produced electron-hole pair or charge-transfer exciton. Our experiments indicate that nonadiabatic transitions must be included in the simulations of the excited state dynamics in low-dimensional CDW solids [7]. Time-resolved spectroscopy should yield important information about these relaxation processes. Recent work on *trans*-polyacetylene has also pointed out the importance of zero-point motion on nonlinear optical properties [25].

The experimental results reported here support the existence of band tail states, reminiscent of the Urbach tail seen in semiconductors, for a 1D CDW material [26]. Of the 1D 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 Ref. [2]. In contrast, tail states observed in materials like *trans*-polyacetylene are most likely dominated by contributions from static structural disorder.

We thank Alan Bishop for pointing out Ref. [2] and its relevance to our experiments. The work at LANL was supported by the U.S. DOE Office of Basic Energy Sciences, Materials Science Division, and the Center for Materials Science at LANL. F.H.L. would like to thank the director's post-doctoral program at LANL for financial support. The work of R.H.M. is supported in part by the DOE, Basic Energy Sciences, Division of Materials Sciences.

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