Intrinsic localized modes in the charge-transfer-solid PtCl

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(August 31, 2018)

Abstract

We report a theoretical analysis of intrinsic localized modes in a quasi-one-dimensional charge-transfer-solid \[\text{[Pt(en)]_2}[\text{Pt(en)}_2\text{Cl}_2](\text{ClO}_4)_4(\text{PtCl})\]. We discuss strongly nonlinear features of resonant Raman overtone scattering measurements on PtCl, arising from quantum intrinsic localized (multiphonon) modes (ILMs) and ILM-plus-phonon states. We show, that Raman scattering data displays clear signs of a non-thermalization of lattice degrees-of-freedom, manifested in a nonequilibrium density of intrinsic localized modes. Adiabatic lattice dynamics is used in a model two-band Peierls-Hubbard Hamiltonian, including a screened Coulomb interaction between neighboring sites. The Hamiltonian is diagonalized on a finite chain. The calculated adiabatic potential for Peierls distortion of the Cl sublattice displays characteristic non-analytic points, related to a lattice-distortion-induced charge transfer. Possible nonadiabatic effects on ILMs are discussed.

63.20. Ry, 05.45.-a, 05.70.Ln
In this paper we discuss intrinsic localized modes, i.e. multi-quanta bound states, [1] in a halogen-bridged mixed-valence transition metal complex \([Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4\) (en=ethylenediamine), subsequently denoted as \(PtCl\) (see [2] and references therein). \(PtCl\) is a representative of a family of \(MX\)-chain compounds, where \(M\) stands for a transition metal (e.g., Pt, Pd, or Ni) in a mixed-valence (i.e. charge-disproportionated) state and \(X\) is a halogen (Cl, Br, or I). \(PtCl\) consists of a 3-dimensional crystalline array of charged linear chains of alternating metal (\(Pt^{3+}\)) and halogen (\(Cl^-\)) ions, with \((en)_2\) ligands attached to the metals. There are also two \(ClO_4^-\) ions per unit cell to maintain charge neutrality. The structure of \(PtCl\) is given in Fig.1 of [3]. Each \(Cl\) ion has two electrons in the filled \(p_z\) orbital (\(z\) is oriented along the chain axis). \(Pt\) ions have on average one electron in each \(d^2\) orbital. There are, therefore, three valence electrons or one hole per unit cell. The ground state of \(PtCl\) displays a very strong charge density wave (CDW) structure. Holes are redistributed to produce an alternating sequence of nominally \(Pt^{2+}\) and \(Pt^{4+}\) ions that have nearly zero and two holes, respectively. \(Cl\) ions then move strongly closer to \(Pt^{4+}\) atoms. As a result of this periodic lattice distortion, hopping matrix elements from \(Pt^{4+}\) ions increase and holes gain energy by virtual hops from \(Pt^{4+}\) to \(Cl\). This strong Peierls-distorted-disproportionation phase is well described by \(Cl - Pt^{4+} - Cl\) trimers, alternating with weakly coupled empty \(Pt^{2+}\) sites: The \(Pt^{4+}-Cl\) distance is 2.318 Å, and the \(Pt^{2+}-Cl\) distance is 3.085 Å. The electron-electron repulsion \(U\) on \(Pt\) sites is not sufficient to destroy the CDW phase or to significantly reduce its magnitude. Therefore, it is not necessary to explicitly include correlations as far as the magnitude of the CDW is concerned. Indeed, as shown in [4], one may introduce effective free-electron model parameters that give correct values for the ground state uniform Peierls distortion. However, calculations in [2], and our calculations below, show that it is necessary to introduce \(U\) if one wishes to describe electronic properties. The optical absorption of \(PtCl\) has two peaks, at approximately 2.5 eV and 5.5 eV, corresponding essentially to \(Pt^{4+} - > Pt^{2+}\) and \(Pt^{4+} - > Cl\) local charge transfer excitons [2]. The width of the \(Pt^{4+} - > Pt^{2+}\) band is of order of 0.7eV [4]. This corresponds to a tunneling time of about \(5.9 \cdot 10^{-15}\) seconds for a hole to tunnel from one
$Pt^{+2}$ site to a near-neighbor one. Due to the large Peierls distortion, the inter-valence charge transfer (IVCT) gap is large, \( \approx 2.5 \text{ eV} = 2.9 \cdot 10^4 \text{K} \). The energy \( E_{ph} \) of the wavevector \( k = 0 \) optical phonon in the system is 38 mEv = 437 K. The period of a phonon oscillation is thus equal to \( 1.4 \cdot 10^{-13} \text{s} \).

Resonant Raman scattering (RRS) measurements on \( PtCl \) were reported in [1], and the observed strong red-shift of overtones interpreted convincingly in terms of multiphonon bound states, i.e., intrinsic local modes (ILMs). Below, we adopt a simple Brownian motion picture of a RRS event, see Fig.1. We first consider the simplest and most probable scenario in the local (atomic) limit appropriate for \( PtCl \). In the first stage, Fig.1a, a photon is absorbed, and a hole is transferred from a \( Pt^{4+} \) ion to the neighboring \( Pt^{2+} \) ion, creating a pair of neighboring \( Pt^{3+} \) ions. Then, in the simplest situation, after some time the hole recombines, emitting a photon. In more complicated and less probable scenarios a number of further hops (tunneling steps) may occur before the recombination. Let us first consider the simplest scenario above. After a hole is transferred to the empty \( Pt \) site the \( Cl \) ion between two \( Pt^{3+} \) sites is no longer in the minimum of its adiabatic energy. Therefore, it starts to move, transferring the electronic energy to the energy of the lattice, Fig.1b. After some time the hole hops back and a photon is emitted, Fig.1c. Some energy remains in the lattice vibration, Fig.1d. This energy corresponds to a quantized intrinsic localized mode (ILM). The quantum ILM energy levels are then observed as peaks in the RRS spectrum [1]. Measurements in [1] also found small magnitude ILM-plus-fundamental side-peaks. These correspond to more complicated situations, when dynamics of at least two neighboring trimers are involved. One of the trimers is excited into an N-phonon state, and the other one is in a one-phonon state. The amplitude of the corresponding peaks is much less than the amplitude of pure ILM peaks [1]. This fact is readily explained in the local picture of a RRS event described above. Dynamics of two trimers may become excited by multiple-hop events. These multiple-hop events have much less probability than the event in Fig.1, due to the very high degree of localization in \( PtCl \) because of its very strong charge disproportionation [1,2]. An important issue is why, if two-trimer excitations do occur, they appear as (N-
1,1) modes, such that there are \( N - 1 \) phonons on one trimer, and one phonon on the other. Other possible modes, for instance (N-2,2) modes are apparently not observed in the RRS spectrum within the experimental resolution [1]. The answer to this puzzle seems to be in the bosonic nature of phonons. Bosons tend to bind together, or "condense", into composite states. The expression for the probability amplitude for a boson to branch to some quantum state has a multiplication factor \( \sqrt{M + 1} \), where \( M \) is the number of bosons already in this state. Therefore, if \( N \) phonons are emitted by an exciton and are allowed to branch into two states (in our case two neighboring trimers), the largest probability is for all of them to go to the same trimer, and then the next most probable configuration is the (N-1,1) configuration. We reiterate that the validity of the whole picture described above is based upon the strongly localized nature [1] of PtCl, i.e., upon the fact that being on a particular trimer is close to a well defined quantum state. As noted above, the energy of the \( k=0 \) optical phonon in PtCl is 437 K. Measurements [1] were performed on samples cooled to 12 K. Even allowing for some local heating of the sample by the laser light, it is impossible that the temperature of the sample during the measurements becomes close to the thermal excitation threshold of optical phonons. Therefore, there cannot be thermalized optical phonons in the system. In spite of that, measurements [1] revealed clearly pronounced "ILM-plus-fundamental" features. These features are anti-Stokes-like lines, corresponding to a transformation of a pre-existing optical phonon into an ILM by an absorption of a photon. This means that the system clearly has pre-existing optical phonons and is, therefore, not in thermal equilibrium. In order for such a non-equilibrium phenomenon to be possible, optical phonons should have a long lifetime, namely the condition \( \tau_{\text{phonon}} G \sim 1 \) should be satisfied, where \( G \) is the number of photons absorbed in the sample per second per unit PtCl cell. A detailed study of this interesting phenomenon requires further experiments, particularly of the anti-Stokes component of the RRS spectrum. It is worthwhile noting that non-thermal phonon distributions have been invoked recently in other strongly coupled electron-phonon materials (e.g. conjugated polymers and proteins [5–7]). Also the long, multitimescale relaxation of classical ILMs has been observed in numerical simulations [8].
on nonlinear lattices.

The usual adiabatic parameter, which is the ratio of characteristic phonon and electron frequencies is small in PtCl. Therefore, the amplitude of Peierls distortion should be well described in the adiabatic approximation. On the other hand, as was shown in [9], the purely adiabatic theory fails to describe dynamic optical absorption attributed to breathers. This is related to the fact that, although the adiabatic approximation may well describe the amplitude of the wave function, it fails to correctly incorporate phase effects. The phase of the wave function does not play a role if one calculates the amplitude of the Peierls distortion, since this calculation seeks the minimum of the adiabatic energy and is phase-insensitive. However, phase effects play a direct role in, e.g., the optical absorption, where effects of constructive and destructive interference are present. One goal of our work here was to check the limits of validity of the adiabatic approximation for the calculation of energies of quantum ILM’s. Our conclusion is that, although the adiabatic approximation can work well for a calculation of the linear part of the energies, it may fail if one calculates the nonlinear corrections, which correspond to the binding energies of phonons in bound states. Since these binding energies are typically small, they may be strongly influenced by non-adiabatic effects.

A minimal phenomenological model to describe qualitative features of PtCl is the two-band Peierls-Hubbard model, introduced for this purpose in [2]. The ingredients of this model are the bond-length-dependent onsite energy difference between Pt and Cl orbitals, the bond-length-dependent hopping matrix element between Pt and Cl ions, and the Hubbard repulsion $U$ for electrons on a Pt atom. Lattice degrees-of-freedom are described by the linear nearest-neighbor elastic spring constant $K$. Further studies [3] have shown, that since the Coulomb interaction at the length scale of one lattice constant is not fully screened, there is a need to take this interaction into account, assuming some reduced effective charges on neighboring sites. The Hamiltonian of our model is

$$H = \sum_{l=-\infty}^{\infty} -t_0(1 - \alpha \Delta_l) \left( c_{l,\sigma}^+ c_{l+1,\sigma} + h.c. \right) + U \sum_{l=-\infty}^{\infty} n_{2l,\uparrow} n_{2l,\downarrow} + 1$$
\[ + \sum_{l=-\infty}^{\infty} \left[ \frac{K \Delta^2}{2} + \frac{P^2_{l}}{2m_{l}} \right] + \sum_{l=-\infty}^{\infty} V_{c} \frac{(n_{l} - Z_{l})(n_{l+1} - Z_{l+1})}{R_{l,l+1}} - \sum_{l=-\infty}^{\infty} [-\epsilon + \beta(\Delta_{2l+1} + \Delta_{2l})] n_{2l}. \]

Here \( c_{i}^{\dag}, c_{i} \) are electron creation and annihilation operators, \( t_{0} \) is the \( Pt \leftrightarrow Cl \) transition amplitude, \( \alpha \) and \( \beta \) are the electron-phonon couplings strengths, \( \Delta_{l} \) is the bond length change for the \( l \)-th bond, \( U \) is the electron repulsion on \( Pt \) sites, \( \epsilon \) is the energy difference between \( Cl \) and \( Pt \) sites, \( K \) is the linear elastic constant, \( m_{l} \) is the mass of the \( l \)-th atom, \( V_{c} \) is a phenomenological parameter related to the charge screening, and \( Z_{l} \) is the positive ion charge at the site \( l \). We assume \( Pt \) sites to take even indices. The filling is three electrons (or one hole) per unit cell. Calculations were performed on 12-site chains, using numerical exact diagonalization and the method of increments described in [10]. The lattice was treated adiabatically. The coupling constants were chosen to fit experimental results for the magnitude of the Peierls distortion, positions and magnitudes of \( Pt^{4+} \rightarrow Pt^{2+} \) and \( Pt^{4+} \rightarrow Cl \) optical absorption peaks, and the optical phonon frequency. Then the nonlinear adiabatic potential for \( Cl \) was calculated by fixing the Peierls-distorted positions of all sites except one \( Cl \) atom, and calculating the energy of the full system as a function of the position of this chosen \( Cl \) atom, see Fig.2a. The displacement \( X \) is measured from the undistorted phase. Positive \( X \) means a displacement in the direction of the \( Pt^{2+} \) site. The minimum of the potential is \( X = -0.37 \AA \), which is the value of the Peierls distortion. At \( X = 0.17 \AA \) the calculated potential has a non-analytic point. At this point the first derivative of the potential with respect to \( X \) has a jump. Physically this non-analytic point corresponds to a transfer of a hole from the \( Pt^{4+} \) site to the closest \( Pt^{2+} \) site. The mechanism of this transfer is as follows. As \( X \) increases, the electron-phonon coupling leads to an energy increase at the \( Pt^{4+} \) site. Two holes on the \( Pt^{4+} \) site experience the Hubbard repulsion. At \( X = 0.17 \AA \) the Hubbard repulsion dominates and one hole is transferred to the closest \( Pt^{2+} \) site. In this situation, the potential suddenly softens. This effect is related to the potential formation of a local kink-antikink pairs in the system, which is illustrated in Fig. 2b. In this figure we plot the adiabatic energy for two \( Cl \) atoms symmetrically displaced. We
observe a local minimum in the adiabatic energy, which should be attributed to the creation of a kink-antikink pair. Having the adiabatic potential, Fig.2a, nonlinear corrections to quantum levels of a Cl$^{37}$ site oscillating in this potential may be accurately calculated using perturbation theory for a quantum anharmonic oscillator [11]. First we performed our calculations without the Coulomb term and found the nonlinear softening of the potential to be seriously underestimated. We were not able to reproduce the experimental values for the nonlinear corrections with any reasonable choice of model parameters. One can view this fact as a confirmation of the importance of intra-chain Coulomb interactions in PtCl$^3$. We then added the Coulomb term and were able to fit the measured values of nonlinear corrections by the following set of model parameters: $t_0 = 0.75$ eV, $U = 2.44$ eV, $\beta = 1.77$ eV/Å, $\alpha = 3.55$ eV/Å, $\epsilon = 0.90$ eV, $K = 9.7$ eV/Å$^2$, $V_c = 8.18$ eV·Å. Our value of the Hubbard $U$ is close to $U = 2.0$ eV, obtained in [3] by quantum chemical configuration interaction calculations on a Cl$^-$Pt$^-$Cl$^-$ cluster. This correspondence is reasonable, since the Hubbard U is characteristic of a highly localized $d$ orbital, and should not change much when going from an atomic cluster to a crystal. The value of the Coulomb repulsion coefficient $V_c$ has the same order of magnitude as the value 13.3 eV·Å found in [3] using a Hartree-Fock approach. The adiabatic potential Fig.2a is quadratic near the equilibrium point and may be written as $E_{ad} = F_1 dx^2/2 + F_2 dx^3/3 + F_3 dx^4/4$. The quantum levels for the Cl atom moving in this potential well are then given by the approximate expression [11]

$$E_n = \hbar \omega \left[ (n + 1/2) + \left( \frac{\epsilon_1}{\hbar \omega} \right)^2 A_n^{(2)} + \frac{\epsilon_1}{\hbar \omega} B_n^{(1)} - \left( \frac{\epsilon_1}{\hbar \omega} \right)^2 B_n^{(2)} \right]. \quad (2)$$

Here $A_n^{(2)} = \frac{15}{4}(n^2 + n + \frac{11}{30})$, $B_n^{(1)} = \frac{3}{4}(2n^2 + 2n + 1)$, $B_n^{(2)} = \frac{1}{8}(34n^3 + 51n^2 + 59n + 21)$, $\omega = \sqrt{F_1/2m}$, $l = \sqrt{\hbar/m\omega}$, $\epsilon_1 = l^3 F_2/3$, $\epsilon_2 = l^4 F_3/4$. In Fig.3 we have plotted the results for energy levels shifts, together with experimental RRS results for PtCl$^{37}$. Here $N$ is the number of phonons in the bound state. For small $N$ we find good agreement with the experiment. At $N = 5$ the amplitude of the shift becomes larger, than our estimates. This suggests to an additional softening nonlinearity in the system at sufficiently large amplitudes. It may be that this nonlinearity is related to nonadiabatic effects, which become
more important as the amplitude of the ILM increases.

To conclude, intrinsic localized modes (ILMs) in PtCl give an example of nonlinear, thermally non-equilibrium excitations in crystal lattices. Similar phenomena, probably related to energy localization and non-thermalization, have been experimentally observed, especially via ultrafast spectroscopy, in several electron-phonon coupled systems. These systems include polymers [3], glasses [6] and biological systems such as proteins [7]. The unique advantage of PtCl and related MX materials is that one can obtain very good crystals with a known structure and controllable and tunable nonlinearity strengths. Therefore, PtCl provides an ideal opportunity for making quantitative models and testing theories of intrinsic nonlinear energy localization (as well as extrinsic energy localization [12]). In this paper, a two-band Peierls-Hubbard model with screened Coulomb interaction, in the adiabatic approximation, has been applied to PtCl. We have found that this gives a good qualitative account of the main phenomena related to the existence of intrinsic localized modes in PtCl, at least for small numbers of bound quanta. We have also shown, that the screened Coulomb interaction is a necessary ingredient within the adiabatic model to explain the quantitative magnitude of nonlinear shifts in the resonant Raman spectrum. We have observed that there exists an additional source of softening in the system at sufficiently large amplitudes. We suspect this is related to non-adiabatic effects; future investigations will be focused on a quantitative theory of these effects. Other important directions for future experimental and theoretical research include measuring life-times of quantum ILMs, understanding intrinsic mechanisms for their decay and their interactions with impurities, as well as studying photoexcited ILMs [13]. PtCl offers the first controlled experimental possibility to investigate these fundamental questions with wide consequences for energy localization and transport in strongly correlated hard, soft, and biological electronic materials.

We are grateful for stimulating discussions with S. Aubry, A. Shreve, B. Swanson and C. R. Willis. Work at Los Alamos is supported by the U.S.D.o.E, under contract W-7405-ENG-36.
FIGURE CAPTIONS

Fig.1: A simple picture of a resonant Raman scattering event in the localized (atomic) limit.

Fig.2: (a) Adiabatic potential for a single $Cl$ atom. The zero of energy corresponds to the equilibrium position in the Peierls-distorted phase. $X$ is the shift of the $Cl$ atom, measured from the undistorted phase. (b) Adiabatic potential for two symmetrically displaced $Cl$ atoms in one trimer.

Fig.3: The absolute value of the nonlinear energy level shift. Dots correspond to the theoretical prediction. Circles are the experimental results for $PtCl_{37}$ [1]; the size of a circle gives the experimental uncertainty due to a finite RRS peak width. Lines are guides to the eye.
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Fig. 1
