Origin of the fine structure in the vibrational spectrum of [Pt(C$_2$H$_8$N$_2$)$_2$][Pt(C$_2$H$_8$N$_2$)$_2$Cl$_2$](ClO$_4$)$_4$: Vibrational localization in a quasi-one-dimensional system

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The complex fine structure in the Raman spectrum of the quasi-one-dimensional solid [Pt(C$_2$H$_8$N$_2$)$_2$][Pt(C$_2$H$_8$N$_2$)$_2$Cl$_2$](ClO$_4$)$_4$ is shown, through studies of isotopically enriched materials and lattice-dynamics calculations, to originate from vibrational modes strongly localized by the positional disorder of the two naturally occurring Cl isotopes, making this an elegant example of a real material displaying vibrational localization in one dimension. The modes responsible for the observed features reside on short chain segments defined by a few statistically favored sequences of isotopes.

The MX chain solids, consisting of alternating transition-metal complexes and halide ions, have recently received much attention as prototypic low-dimensional charge-density-wave (CDW) solids.[1] A particularly well-studied class are compounds of the form [Pt(en)$_2$][Pt(en)$_2$X$_2$](ClO$_4$)$_4$, (en=ethylenediamine), generally referred to as PtX(X=Cl,Br,I). These highly anisotropic semiconductors are generally Peierls distorted, with the halogens displaced from the central position between the metal complexes, and the metals in alternating valence states best described as a commensurate CDW. This versatile class of highly correlated electronic materials provides an opportunity to manipulate the balance between electron-phonon and electron-electron interactions and tune the strength of the CDW, either chemically or through the application of pressure. They span a wide range of behaviors, from the strong-CDW, highly Peierls-distorted regime of PtCl, through the weakly distorted PtI, to the nondistorted, possibly spin-density-wave case[2] of [Ni(R,R-chxn)$_2$Br]Br$_2$ (chxn =cyclohexane diamine). With this versatility, their crystalline nature, and the ability to obtain clear spectral signatures of photoinduced gap states (polarons, excitons, kinks, etc.), these materials have emerged as model systems for testing theories of one-dimensional solids.[1]

The extent to which PtCl and other Cl-bridged compounds are well-ordered systems, however, has been called into question by the puzzling observation of a complex fine structure in the Raman spectrum of the Cl-M^{IV}-Cl symmetric stretch (ν_1) chain phonon. Several groups have resolved the ν_1 mode of several M-Cl compounds into triplet[3,4] or quintet[5] structures. An early explanation of the fine structure based on Cl isotope splittings[4] was generally rejected due to poor agreement between prediction and experiment. Analysis of the fine structure by Tanaka and Kurita[5] suggested that these features have their origin in distinct correlation lengths of the MX chains, an interpretation implying high densities of intrachain defects that would severely complicate the analysis of physical properties.

Here we demonstrate conclusively, through studies of isotopically enriched Pt^{35}Cl, that the complex structure

in the ~ 308-cm^{-1} ν_1 mode is, in fact, a Cl isotope effect. The nature of the modes responsible for the various peaks, moreover, is of fundamental interest. Lattice-dynamics calculations for a simple linear chain model, reproducing the observed spectra with remarkable accuracy, show that the slight disorder induced by randomly distributed ^{35}Cl and ^{37}Cl isotopes is sufficient to cause the vibrational modes of the chains to become highly localized and that the discrete fine structure originates from modes confined to "islands" formed by a few specific sequences of ^{35}Cl and ^{37}Cl isotopes occurring with high probability. It emerges that PtCl is a physical realization of the classic case of a two-component one-dimensional (1D) chain with positional disorder, a traditional starting point for theories of vibrations in disordered solids, and provides experimental verification of long-standing predictions for this 1D case.[6-8]

To synthesize $\sim 99\%$ ^{35}Cl enriched PtCl, unenriched PtCl is first prepared according to a standard method.[9] The red crystals (0.05 g, 0.045 mmol) are dissolved in H$_2$O (5 mL) along with Na^{35}Cl (0.26 g, 4.5 mmol) obtained from Oak Ridge National Laboratory, and the solution maintained at 40 °C for 6 days. HClO$_4$ (~ 2 mL) is added at room temperature to precipitate the enriched PtCl, which is recrystallized from H$_2$O over 4 days to obtain crystals up to $20 \times 2 \times 1$ mm^3. A second synthetic route, in which ^{35}Cl enrichment was attempted with ^{35}Cl$_2$ gas, resulted in slightly enriched crystals containing roughly 15% ^{37}Cl, compared to 25% for natural abundance.

Isotopic abundances are estimated from far-infrared (FIR) transmission spectra. The IR-active ν_2 mode exhibits an isotopic fine structure, simpler than ν_1's, consisting of three peaks,[10] at 359.1, 356.5, and 352.9 cm^{-1} [or at 355.8, 352.5, and 348.8 cm^{-1} when perdeutero-(en) is used], whose relative strengths were judged a good measure of the Cl isotopic abundances. FIR spectroscopy of MX materials with various isotopic substitutions is the subject of a forthcoming publication.[10]

Raman spectra are obtained from single crystal samples maintained at 13 ± 2 K with laser excitation (<20 W/cm^2) provided by an Ar$^+$ laser or an Ar$^+$-pumped
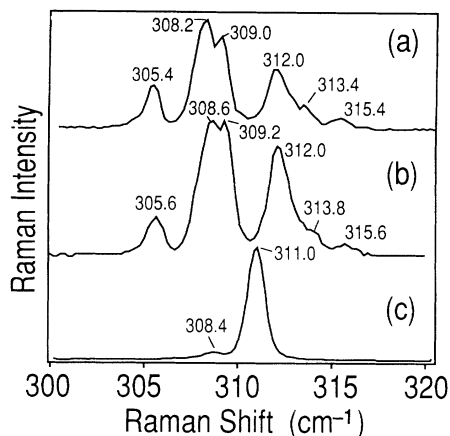
FIG. 1. Raman spectra in the ν_1 region of PtCl at 13-K, 2.41-eV excitation. (a) Natural Cl isotopic abundance (75:25 ^{35}Cl:^{37}Cl). (b) Lightly ^{35}Cl enriched (85:15 ^{35}Cl:^{37}Cl). (c) 99% ^{35}Cl enriched (grown at 40 °C). Incident and scattered light are polarized parallel to the chain axis.

Ti:sapphire solid-state laser for 514.5 or 750-nm excitation, respectively. Scattered light is coupled into a scanning double monochromator operating at 0.4-cm^{-1} resolution, equipped with a thermoelectrically cooled photomultiplier. Both incident and scattered light are polarized parallel to the chain axis.

Since we have recently shown[11] that PtCl undergoes a structural phase transition at 19 °C, we perform our measurements on crystals grown and maintained in the low-temperature monoclinic phase. The substantial sharpening of the ν_1 peaks, as compared to samples prepared at higher temperatures and cooled through the phase transition, enables us to resolve at least six distinct features in the ν_1 region. Figure 1 shows the Raman spectra of (a) PtCl with natural Cl isotopic abundance, (b) lightly ^{35}Cl enriched PtCl (85:15 ^{35}Cl:^{37}Cl), and (c) highly (~99%) ^{35}Cl enriched PtCl. For the two samples with substantial ^{37}Cl concentrations, the six major features fall at (a) 305.4, 308.2, 309.0, 312.0, 313.4, and 315.4 cm^{-1} and (b) 305.6, 308.6, 309.2, 312.0, 313.8, and 315.6 cm^{-1}. We find that the relative intensities of the fine-structure components are identical for spectra obtained by exciting 2.41 eV, within the intervalence-charge-transfer (IVCT) band of the material, and at 1.65 eV, well below the IVCT band edge.

The isotopic origin of the ν_1 fine structure is explicitly demonstrated by the spectrum of the ~99% ^{35}Cl enriched material, Fig. 1(c), where the complex fine structure collapses to single strong mode at 311 cm^{-1} with a weak shoulder at 308.4 cm^{-1}.

Isotope effects were previously rejected[3-5] as an explanation for the ν_1 fine structure because early arguments were based on an oversimplified Cl-Pt^{IV}-Cl local oscillator model. This predicts only three components with relative intensities of 9:6:1, in stark contrast to experiment, with the ^{35}Cl-Pt^{IV}-^{37}Cl and ^{37}Cl-Pt^{IV}-^{37}Cl modes at 307.4 and 303.5 cm^{-1} (assuming the 312-cm^{-1} feature arises from ^{35}Cl-Pt^{IV}-^{35}Cl), substantially lower than the closest observed features at 308.2 and 305.4

cm^{-1}.

The experimental results, however, can be reproduced extremely well in a simple 1D lattice-dynamical treatment based on a linear chain (Cl-Pt^{IV}-Cl $\cdots$ Pt^{II} $\cdots$)$_n$, with harmonic springs.[12] Nearest-neighbor springs, K_1 (for Pt^{IV}-Cl interactions) and K_2 (for Pt^{II}-Cl), are sufficient to reproduce the Raman results. To interpret the results it is helpful to recall the well-known result that substitutional mass defects give rise to new vibrational modes localized at the defects.[6] For a two-component chain, substitution for the lighter component (Cl in this case) gives rise to either a local mode above the optic branch or to a gap mode below it, depending on whether the substituted atom is lighter or heavier than the original, respectively. In both cases, localization increases with the mass difference between the substituted and original atoms. The local mode evolves out of the highest optic phonon in the branch (zone boundary in this case) while the gap mode evolves from the lowest (zone center), and they retain some of those phonons' character if the substituted atom is close in mass to the original. These modes can have frequencies quite different from those of any optically active phonon. For example, since the local mode must lie above the highest phonon in the branch, its frequency can be much higher than the zone-center phonon for a chain formed from just the light impurities, depending on the dispersion of the branch.

Since the highly enriched Pt^{35}Cl can be thought of as perfect Pt^{35}Cl chains with dilute ^{37}Cl defects, assignments of the two observed Raman peaks based on these ideas can be made with confidence. With the Peierls distortion of the PtCl chains, it is more natural in this case to think in terms of substituting Cl-Pt^{IV}-Cl units rather than single Cl atoms; we shall abbreviate these units by referring only to the Cl isotopes surrounding the Pt^{IV} (e.g., a "35-37 unit"=^{35}Cl-Pt^{IV}-^{37}Cl). It is clear that the strong 311.0-cm^{-1} feature is the zone-center ν_1 phonon for a nearly perfect Pt^{35}Cl chain, while the weak 308.4-cm^{-1} feature is the gap mode arising from 37-35 defects. Nearby 35-35 units participate in the gap mode, driving its frequency higher than that of an isolated 37-35 unit.

For PtCl with 25% or 15% ^{37}Cl the extremely high heavy isotope density means it is no longer entirely appropriate to think in terms of isolated defects on otherwise perfect chains, and it is here that explicit calculations facilitate further understanding. To simulate Raman spectra of various isotopic mixtures, we calculate the normal mode eigenfrequencies and eigenvectors for a finite chain, typically 32 unit cells (128 atoms), with cyclic boundary conditions. This is done in the standard manner, by diagonalizing the appropriate dynamical matrix.[6] We begin with a pure Pt^{35}Cl chain and a chain with a single ^{37}Cl defect. The spring constants are adjusted so that the model yields results consistent with experiment for the 99% ^{35}Cl sample; i.e., the zone-center ν_1 phonon for the pure Pt^{35}Cl chain falls at 311.0 cm^{-1}, and the gap mode for dilute 37-35 defects in a Pt^{35}Cl chain falls at 308.4 cm^{-1}. The second condition requires in effect that the ν_1 branch disperse upward by 6.5 cm^{-1} from zone center to boundary. Both conditions can be

satisfied using just the two nearest-neighbor force constants. Two further conditions imposed by the IR results—that the ν_2 phonon fall at the observed frequency and that, to make the ν_2 fine structure collapse into the observed three peaks, the dispersion of the ν_2 branch be less than about 3 cm^{-1}—require the inclusion of second-nearest neighbor interactions K_3 and K_4 for the two kinds of Cl-Cl interactions, and a relatively large K_5 for the Pt^{II}-Pt^{IV} interaction. These conditions do not uniquely determine the set of force constants, but any set satisfying them yields essentially the same spectra. Here we use either $K_1 = 134.6$, $K_2 = 66.3$ N/m, $K_3 = K_4 = K_5 = 0$ (to fit only the Raman results) or $K_1 = 165$, $K_2 = 45$, $K_3 = K_4 = -2.3$, and $K_5 = 36$ N/m (to fit both the Raman and IR results.)

The problem is then solved, using the same springs, for chains with randomly distributed Cl isotopes, in which the occupation of a given site by ^{35}Cl or ^{37}Cl is determined by a random number generator. In order to attain good statistics without diagonalizing inordinately large matrices, we solve one hundred 128-atom random chains, rather than a single long chain, and combine the results in the simulated spectra. Raman spectra are simulated by assigning a Lorentzian line shape of fixed width (0.8 cm^{-1} full width at half maximum) to each normal mode and summing over all modes. The Raman cross section for each eigenvector is estimated by considering only the Pt^{IV}-Cl bonds, setting their polarizability change proportional to the change in bond length and summing over all bonds.

Simulated spectra for chains with 25%, 15%, and 1% randomly distributed ^{37}Cl are shown in Fig. 2. Comparing with Fig. 1 one finds remarkably good agreement with the observed spectra, with the six major and even the various minor peaks all reproduced.

Examination of the eigenvectors obtained from this model reveals that the observed spectral features result from highly localized vibrational modes isolated on a few specific sequences of ^{35}Cl and ^{37}Cl isotopes which occur with high statistical probability. The isotope sequences and atomic displacement patterns associated with the six
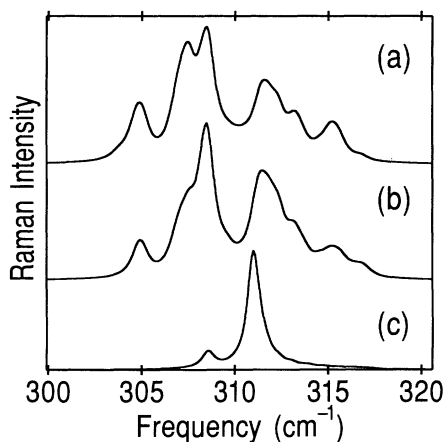

FIG. 2. Raman spectra predicted from the lattice-dynamics calculations for 1D chains with randomly distributed ^{35}Cl and ^{37}Cl isotopes. (a) 25% ^{37}Cl. (b) 15% ^{37}Cl. (c) 1% ^{37}Cl.
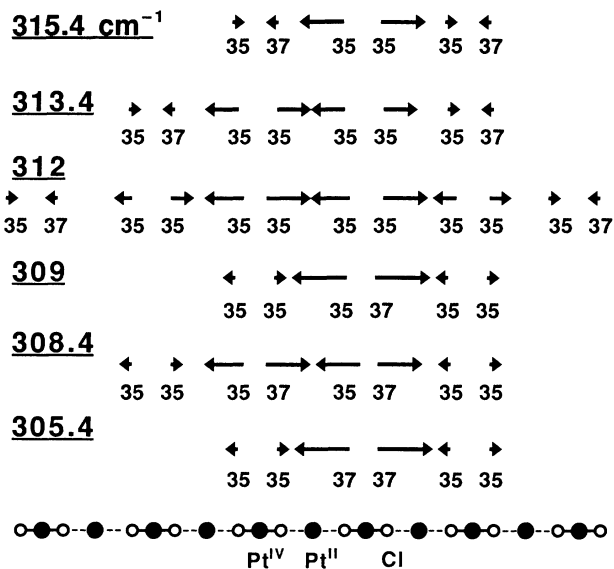

FIG. 3. Eigenvectors for the localized modes responsible for the six strongest Raman peaks. Cl displacements are shown along with the Cl isotope sequence associated with each mode. The PtCl chain is shown at bottom.

most strongly Raman-active local modes are shown in Fig. 3. The intensities of the various Raman features are dictated by a combination of the probability of occurrence for the associated isotope sequence, and of the Raman cross section for the mode localized on that sequence.

Qualitative insight into the nature of several of these modes can be gained by noting that, because the vibrational amplitude for each mode is concentrated on just a few unit cells, the character of a mode centered on a given Cl-Pt-Cl unit is determined almost entirely by the Cl isotopes on the nearest- and next-nearest-neighbor units surrounding it. Thus, to a good approximation, these modes act as if they were localized on isolated defects in an infinite chain of a type defined by the immediate neighborhood of the center unit. For example, the simplest of the highly probable sequences include a 37-37 or 35-37 unit surrounded on both sides by 35-35. These give rise to modes whose character can be approximated quite well by the corresponding gap modes for dilute 37-37 or 35-37 defects in a 35-35 chain. The features at ~ 305.5 and ~ 309 cm^{-1}, respectively, correspond to modes of this type. Similarly, the mode at 315.4 cm^{-1} corresponds to a 35-35 unit surrounded by 35-37 units (the ordering of the isotopes within the 35-37 units has very little effect on the character of the mode), which can be approximated by the local mode for a 35-35 defect in an otherwise perfect 35-37 chain.

Of the remaining features, the strong peak at ~ 308.4 cm^{-1} corresponds to a pair of 35-37 units surrounded by 35-35s, while the weak at 313.4 cm^{-1} corresponds to a pair of 35-35 units surrounded by 35-37s. Finally, the strong, broad peak at 312 cm^{-1} arises from various short segments of pure ^{35}Cl chain, i.e., three, four, five, or more consecutive 35-35 units, terminated on either end by 35-37 or 37-37; a four-unit segment is shown in Fig. 3. Since

these ^{35}Cl segment modes are similar in character to finite-wave-vector phonons for the pure chain, their higher frequency compared to the zone-center phonon of the pure chain makes intuitive sense given the upward dispersion of the ν_1 branch.

Highly localized behavior occurs in PtCl even with such a small (5.4%) difference in isotope masses because the strongly Peierls-distorted structure, and the concomitant large difference between K_1 and K_2, already puts the system close to localization on the Cl-Pt^{IV}-Cl units. With more nearly equal force constants, localization would be much less pronounced and the modes would involve much longer isotope sequences, with the result that the spectra would have many closely spaced peaks which likely would merge into a single band.

Thus PtCl is a fortuitous case. In most solids, the small amount of disorder resulting from randomly distributed isotopes is not sufficient to yield vibrational modes localized to the extent that they are experimentally distinguishable from ordinary extended phonons. Though complex structure in the vibrational density of states, arising from localization of vibrational energy on "islands," was predicted in numerical simulations on random 1D chains over thirty years ago,[6-8] no real 1D systems were known to which these early results could be applied directly. Rather they were used, with varying success, as a starting point for understanding 3D disordered solids. To our knowledge, PtCl is the first 1D material to provide direct experimental verification of these predictions. PtCl is a striking example of a real solid which can be accurately modeled in 1D, and for which isotopic disorder leads to such complete and clearly manifested vibrational localization.

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