RESONANCE RAMAN AND FAR-INFRARED STUDIES OF ISOTOPICALLY DISORDERED AND MIXED-HALIDE HALOGEN-BRIDGED PLATINUM CHAIN SOLIDS

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ABSTRACT

The MX chain solids $[Pt(en)_2][Pt(en)_2X_2](ClO_4)_4$, (en = $C_2H_8N_2$ and X=Cl, Br), referred to as "PtX," are used to explore some of the surprising spectral consequences of disorder in 1-D systems, first for pure PtCl, where the disorder arises from randomly distributed Cl isotopes, then for the more drastic case of the mixed-halide materials $PtCl_{1-x}Br_x$. Lattice dynamics and Peierls-Hubbard modelling are used to analyze the observed spectral behavior. In both cases, the complex structure seen in the Raman and IR spectra is found to arise from strongly localized vibrational modes residing on chain segments, defined by sequences of Cl isotopes for PtCl, and by sequences of Cl and Br for $PtCl_{1-x}Br_x$.

INTRODUCTION

Solids of the form $[Pt(en)_2][Pt(en)_2X_2](ClO_4)_4$, (en = $C_2H_8N_2$ and X=Cl, Br, or I), generally referred to as "PtX," are among the most widely studied members of the MX class of low-dimensional solids. These materials are characterized by weakly interacting one-dimensional metal–halide chains, with the metals in alternating valence states best described as a commensurate charge density wave, and display an intense, highly anisotropic optical absorption associated with the metal-metal intervalence charge transfer (IVCT). The MX materials have recently emerged as nearly ideal systems for testing theories of a wide range of low-dimensional phenomena. Here we use the MX materials to explore some of the surprising consequences of disorder in 1-D on vibrational spectra, first for pure PtCl, where the disorder arises from randomly distributed Cl isotopes, then for the more drastic case of the mixed-halide materials $PtCl_{1-x}Br_x$. Recognizing that the observed complex spectral structure is a consequence of a particularly simple form of disorder and understanding the details of how such structure arises has permitted the resolution of several long-standing puzzles about these materials.

VIBRATIONAL CONSEQUENCES OF DISORDER IN ONE DIMENSION—AN OVERVIEW

The effect of disorder on the vibrational properties of a solid is one of the classic problems of lattice dynamics. A traditional starting point for theoretical exploration of this problem has been the random two-component linear chain, in which the two components are treated as isotopes in the sense that they differ only in mass, with interatomic forces remaining identical. Early computer simulations on such systems yielded an intricate fine structure in the vibrational density of states, consisting of a multitude of sharp peaks, which surprisingly did not smooth out as the number of

atoms in the simulation was increased, even when tens of thousands of atoms were used.[1,2] This ran counter to the intuitive notion that phonons, by their extended nature, should in effect see a long-range average over the two components to produce a relatively smooth spectrum. The physical explanation for this unexpected result was that the disorder led to vibrational modes which no longer can be considered extended phonons, but rather are localized on just a few atoms, and that the various peaks correspond to modes associated with highly probable sequences of the two components. As discussed below, our results for PtCl provide the first direct experimental confirmation of these predictions for a real quasi-one-dimensional solid.[3]

An intuitive understanding of the completely disordered chain can best be gained by approaching the problem in stages. The first stage is to consider a single defect, e.g. an atom of the wrong mass, in an otherwise perfect chain; one then obtains the familiar localized defect modes.[4] For a two-component chain with the defect atom substituting for the lighter component, these defect modes obey the following rule: if the substituted atom is lighter than the original, the defect mode must lie above the highest mode of the associated optic phonon branch, and if it is heavier, it must lie below the lowest phonon in that branch.[4] Thus the dispersion of the associated phonon branch plays a critical role in determining the frequency of the defect mode.

The second stage is to consider the effects of two such defects in an otherwise perfect chain. As before, we will get local modes at each defect. But in addition, the two defects now impose boundary conditions on the segment of chain between them. This leads to a new set of vibrational modes, distinct from the extended phonons and the defect local modes, localized on this chain segment. The segment modes with substantial IR or Raman activity will be those without any nodes within the segment. A first approximation for the frequency to be expected for such modes can be obtained by noting that the atomic displacement patterns of such a mode is quite similar to a piece of a of non-zero wavevector phonon from the associated branch; a segment mode localized on a segment of length d will correspond approximately to a phonon of wavevector π/d. Hence, as was the case for the defect local mode, the dispersion of the associated phonon branch for the perfect chain plays a major role in determining the frequencies of these segment modes.

The case of a completely random mixed chain is essentially a combination of the above effects. For severe enough disorder (large enough mass differences between the mixed components), the vibrational modes are so strongly localized that each segment or defect feels only the effects of its immediate neighborhood, and acts as if it were an isolated segment in a long chain of the type defined by that immediate neighborhood. The observed vibrational spectrum will then be just a few localized modes residing on the segments and defects which occur with the highest probability. (For weaker localization, the length of the relevant segments, and hence and the number of possible types of segment, becomes larger, so that a large number of modes will occur, eventually merging into a broad band.) The particularly simple form taken by the localized modes in 1-D, and their strong dependence on the dispersion of the associated phonon branches, suggests that phonon dispersions can be extracted from an analysis of the local mode frequencies. As will be seen below, this provides a novel way of obtaining phonon dispersion information by purely optical means.

Finally, we note that the frequencies of the segment modes do not depend strongly on the nature of the defects defining the segments. Thus photo-induced electronic defects, which would be manifested as force constant defects, could also lead to segment modes very similar to those formed by mass defects, as long as the electronic defect is strongly localized and occurs in sufficiently high numbers.

LOCALIZATION BY CHLORIDE ISOTOPIC DISORDER IN PtCl

Figure 1 shows the Raman and infrared spectra of PtCl at roughly 20K for the fundamental Cl-Pt$^{III+\delta}$-Cl symmetric stretch (v_1) and asymmetric stretch (v_2) phonon regions. Shown on top are

spectra for samples prepared with natural Cl isotope abundance (75% ^{35}Cl, 25% ^{37}Cl); on the bottom are spectra for samples prepared with ~99% pure ^{35}Cl. Clearly the fine structure seen in the top spectra arises from Cl isotopes, but there are several puzzling aspects. Why, for instance, is the v_1 Raman fine structure so complex compared to the simple three-peaked structure seen in the IR for v_2? And how does the addition of *heavier* isotopes lead to v_1 fine structure components *higher* in frequency than for the pure ^{35}Cl case?
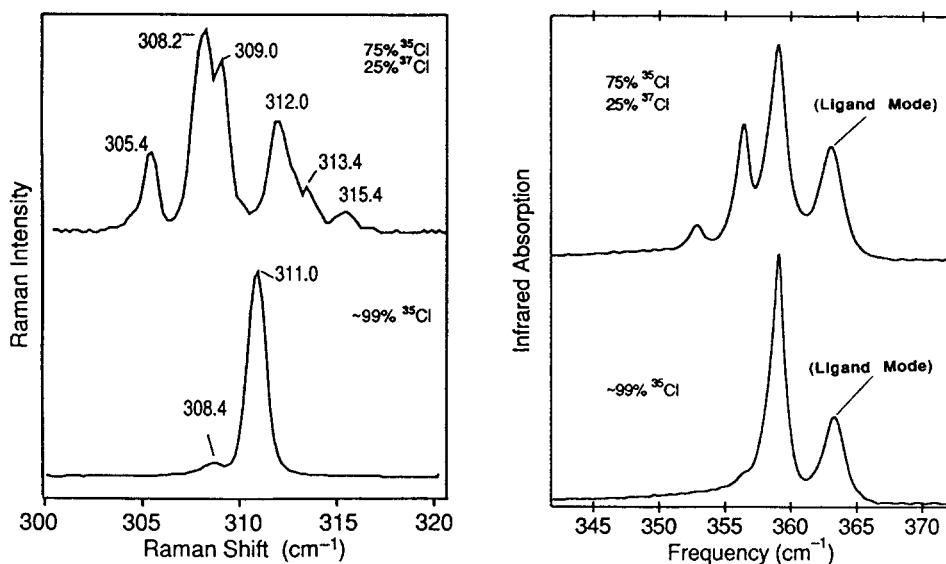

Fig. 1. Experimental Raman and infrared spectra of PtCl at approximately 15 K, for natural Cl isotopic abundance (top) and for ~99% isotopically pure ^{35}Cl (bottom).

All these surprising features are purely lattice dynamical in origin, and can be understood in terms a simple 1-D harmonic mass-and-spring model. Figure 2 shows simulated Raman[3] and IR[5] spectra, obtained from such a model which included only Pt and Cl atoms with first- and second-nearest neighbor interactions. Comparison with Fig. 1 reveals remarkably good agreement. To produce these simulated spectra, the model spring constants were first obtained by fitting the model to the ~99% ^{35}Cl case. This fit included the weak satellite peaks in the experimental spectra, arising from the localized modes of isolated ^{37}Cl "defects;" doing so defined the phonon dispersions for the v_1 and v_2 branches. The eigenfrequencies and eigenvectors were then obtained for a hundred 128-atom chains having randomly distributed ^{35}Cl and ^{37}Cl. The Raman cross-sections and IR dipole moments were calculated for each eigenvector, and the results combined to form the simulated spectra.[3,5]

The model shows that the unusual features of these spectra are a consequence of the surprising fact that even the small mass difference (~5%) between the two randomly distributed Cl isotopes is a severe enough disruption of translational symmetry to put the vibrational modes into the strongly localized regime. As predicted for this case in the previous section, the observed modes are found to reside on short chain segments defined by a few statistically favored sequences of isotopes. Figure 3 shows the isotope sequences and approximate eigenvectors for the six strongest observed Raman peaks; the same isotope sequences give rise to the IR modes.
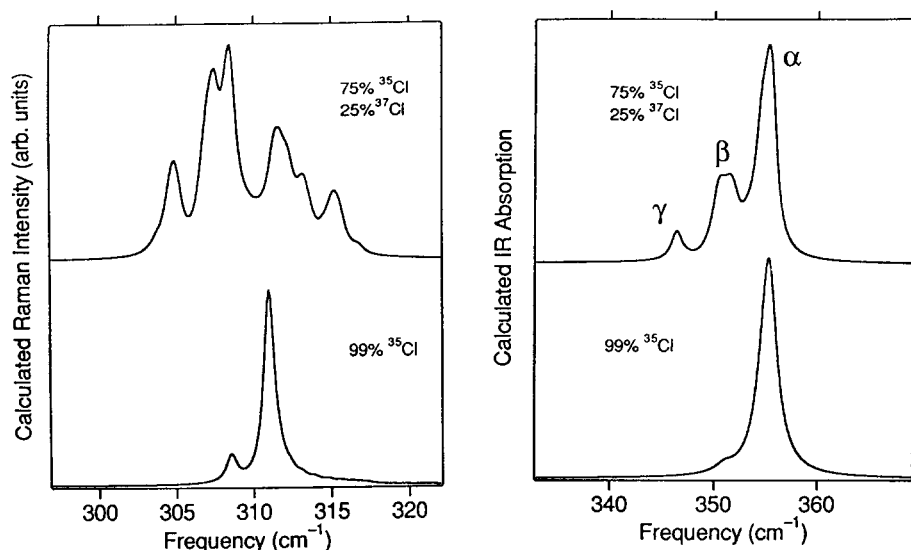
Fig. 2. Raman and infrared spectra of PtCl calculated from the harmonic linear chain model, for natural Cl isotopic abundance (top) and for 99% isotopically pure ^{35}Cl (bottom).
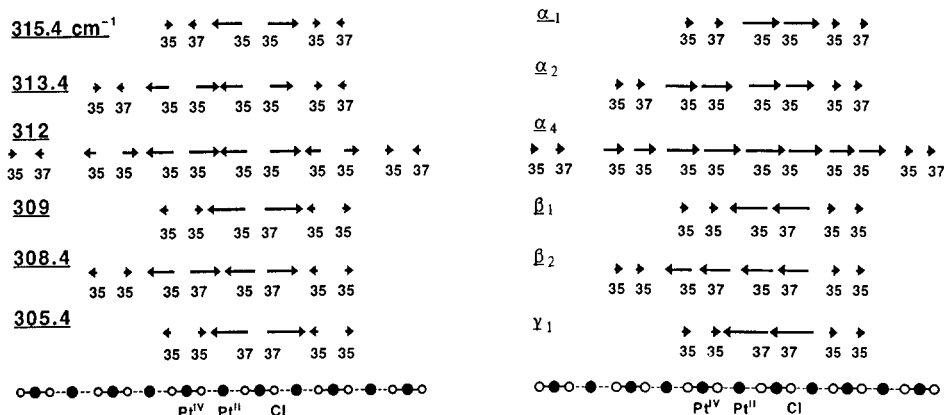

Fig. 3. Cl isotope sequences and approximate atomic displacement eigenvectors for the six strongest Raman (left) and IR (right) localized modes in natural abundance PtCl. For clarity, only Cl displacements are shown. Frequencies for the Raman modes are shown. For the IR, modes labelled α, β, and γ fall within the frequency ranges of the correspondingly labelled features in Fig. 2.

The remarkably different appearances of the observed fine structures for the Raman-active v_1 mode and the IR-active v_2 mode are found to be the result of different magnitudes and directions of dispersion for the two phonon branches, with the v_1 frequency of the isotopically pure material increasing with increasing phonon wavevector by 6.5 cm^{-1} from Brillouin zone center (Γ) to zone boundary (X), while v_2 disperses downward by less than 3 cm^{-1}. Given the upward dispersion of the v_1 branch, the ordering of the modes, with shorter segments corresponding to higher frequency, makes intuitive sense. The question of how adding heavier isotopes can produce higher frequency v_1

components is also answered: the heavy atoms act to define short segments of light-isotope chain, which for upward dispersion have modes higher in frequency than the zone center (infinite chain) phonon. For the v_2 branch, the dispersion is so small that the local modes for all segment lengths cluster closely around the frequencies for ordered $^{35}Cl-Pt^{IV}-^{35}Cl---Pt^{II}$, $^{37}Cl-Pt^{IV}-^{35}Cl---Pt^{II}$, and $^{37}Cl-Pt^{IV}-^{37}Cl---Pt^{II}$ chains.[5]

LOCALIZED MODES IN THE $PtBr_{1-x}Cl_x$ SYSTEM

Compared to pure PtX systems containing a single halide species, the resonance Raman spectra of mixed-halide systems, shown in Fig. 4, are strikingly rich and complex, displaying a multitude of puzzling features not seen in either of the constituent pure PtX materials.[6] The Raman spectra of pure PtCl or PtBr are dominated by the fundamental $X-Pt^{IV}-X$ symmetric stretch (v_1) chain phonon, at 308 or 165.5 cm^{-1}, respectively, which are dramatically enhanced when the excitation energy is near resonance with the IVCT band. In contrast, for the mixed $PtBr_{1-x}Cl_x$ system the 165.5 cm^{-1} mode is replaced a series of lines between 181 and 166 cm^{-1}, each coming into resonance at successively lower excitation energies, so that typically two or three neighboring lines are observed at a given excitation energy, producing an apparent Raman "dispersion".[7] In addition there appears a cluster of modes near 210 cm^{-1} which also show strong excitation dependence, and another cluster near 324 cm^{-1} which are both Raman- and infrared-active.

A systematic spectroscopic study of the $PtBr_{1-x}Cl_x$ system has enabled us to determine that the mechanism for the complex spectral behavior of this system is closely related to that responsible for the isotopic fine structure in pure PtCl, again involving vibrational modes localized on finite segments, this time defined by sequences of Cl and Br rather than by isotopes. The $PtBr_{1-x}Cl_x$ case has the added complication that the PtBr and PtCl segments have different electronic properties,

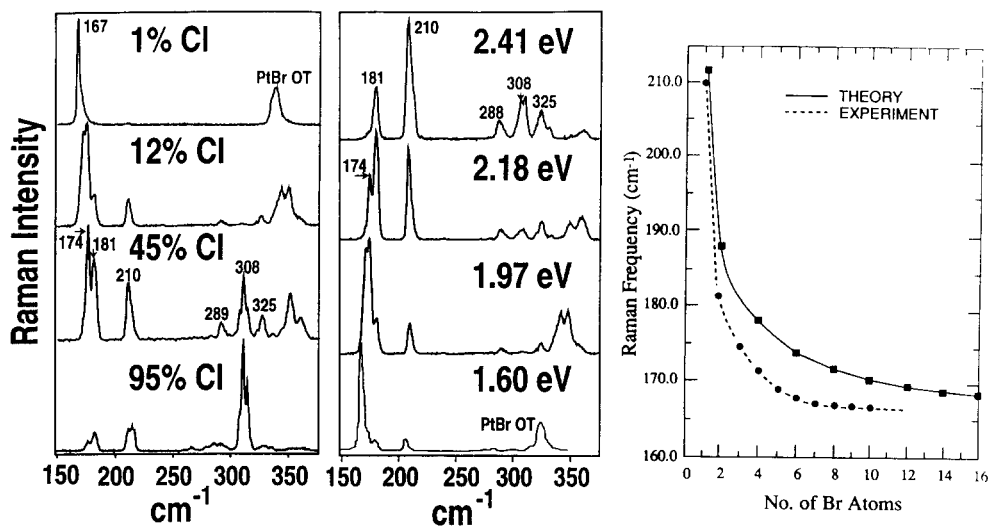Fig. 4. (Left) Cl concentration (x) dependence of Resonance Raman (RR) spectra at 1.98eV for $PtCl_xBr_{1-x}$ crystals. (Center) Excitation dependence of RR spectra of $PtCl_{0.12}Br_{0.88}$. (Right) Calculated and experimental Raman mode frequency as a function of PtBr segment length, including the 210 cm^{-1} interface mode.

leading to different excitation profiles for the various segments, thus necessitating a more detailed theoretical treatment than for the Cl isotope problem.

The frequencies of all the observed features, as well as their composition dependence and excitation profiles, can be accurately predicted in a 3/4-filled two-band Peierls-Hubbard treatment[8] in which the mixed chain consists of interspersed short segments of pure PtBr and PtCl. An important prediction of this model is that the electronic healing length between the PtBr and PtCl segments is very short, so that the interatomic force constants within the short segments are essentially the same as in the corresponding pure material. Thus, vibrationally, we are again in a situation very similar to that of the Cl isotopes of the previous section, but with the disorder much more drastic. The $181–166$ cm^{-1} series arises from the v_1 mode of successively longer segments of PtBr embedded in PtCl, with the 181 cm^{-1} mode corresponding to a single $Br–Pt^{IV}–Br$ unit. The ~210 cm^{-1} and the ~324 cm^{-1} modes arise whenever a PtBr / PtCl junction occurs at a Pt^{IV} site, and correspond to the stretching modes of the $Br–Pt^{IV}–Cl$ unit thus formed, with their exact frequencies depending weakly on the lengths of the associated segments. As in the first section, the eigenvectors for the segment modes of the $181–166$ cm^{-1} series closely approximate PtBr v_1 phonons of various wavevectors. Thus the mixed system results enable us again to indirectly infer the dispersion of this phonon branch as being upward from Γ to X by roughly 50 cm^{-1}.

CONCLUSIONS

We have demonstrated that in both the PtCl Cl isotope and the $PtBr_{1-x}Cl_x$ cases, disorder within the chain leads to vibrational modes localized on finite chain segments, with the vibrational spectra dominated by modes associated with a few statistically favored types of segments. The simplicity of the 1-D case makes it possible to extract phonon dispersions through analysis of the disorder-induced fine structure. These general principles should be relevant for a wide variety of 1-D systems.

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