

Pressure Tuning of the Charge Density Wave in the Halogen-Bridged Transition-Metal (MX) Solid $Pt_2Br_6(NH_3)_4$

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We report the pressure dependence up to 95 kbar of Raman active stretching modes in the quasi-one-dimensional MX chain solid $Pt_2Br_6(NH_3)_4$. The data indicate that a predicted pressure-induced insulator-to-metal transition does not occur, but are consistent with the solid undergoing either a three-dimensional structural distortion, or a transition from a charge-density wave to another broken-symmetry ground state. We show that such a transition can be well-modeled within a Peierls-Hubbard Hamiltonian.

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The halogen-bridged ($X=Cl, Br, I$) transition metal ($M=Pt, Pd, Ni$) compounds (MX solids) have recently attracted a great deal of attention as paradigms of one-dimensional (1-D) systems¹. Unlike conjugated polymers, the MX materials typically consist of linear rather than planar chains, and can be formed as single crystals, therefore mitigating complications in interpreting experimental results obfuscated by disorder. Furthermore, MX systems exhibit a wide variety of broken-symmetry ground states ranging from a strongly Peierls distorted charge-density-wave (CDW) in $PtCl$, to a weak one in PtI , to a spin-density-wave (SDW) in $NiBr_2$; transitions between these states are, in fact, a focus of this paper. Theoretical interest in these materials has also been stimulated by their role as 1-D analogs of high-temperature Cu-O superconductors³.

An MX complex is typically represented by $[ML_4][MX_2L_4]Y_4$, where L is a ligand molecule, such as ethylamine, X represents the bridging halide, and Y is a counterion, such as ClO_4^- . It has been found that the network of ligands and counterions forms a template to which the M and X atoms along the chain must adjust^{4,5}. The result is that the choice of L and Y has a dramatic influence (the “template effect”) on the separation between adjacent M atoms, which appears to determine the Peierls distortion ρ (the ratio of the short to long $M-X$ bond lengths) of the CDW. We have observed⁵ that both the frequency of the Raman-active chain mode ν_1 , associated with the symmetric stretching of the axial X atoms around each M^{4+} atom, and the energy (or charge transfer) gap E_g , increase monotonically as ρ decreases (as the CDW strength increases), demonstrating the utility of simple optical techniques for probing ground state properties. The tunability of E_g is obviously a desirable feature in materials used in optical devices, such as light-emitting diodes⁶.

In addition to chemical substitution, pressure (P) can be used to tune ρ , with Raman spectroscopy as a means of detecting the consequent changes in the geometry of an MX chain through observation of ν_1 . An excellent candidate for high P Raman studies is $Pt_2Br_6(NH_3)_4$ (abbreviated $PtBrn$), an MX solid with neutral chains,

and, hence, a relatively small number of atoms per unit cell (see Fig. 1, Ref. 7). This particular material was the subject of two recent theoretical studies based on local density approximation (LDA) calculations^{7,8}, one of which predicted the onset of metallization at $P_C=89$ kbar, induced by uniaxial stress along the chain axis. The calculations suggested that evidence for this transition would be a continuous decrease of ν_1 to zero as P increased from zero to P_C . Although previous experimental studies indicated that such a pressure-induced metallization is averted in charged MX chains (*i.e.*, $PtCl$ and $PtBr$ with ethylenediamine ligands and ClO_4^- counterions)⁹⁻¹⁴, it is essential to recognize that the local chemical environments of the charged and neutral chains are significantly different from each other. The importance of the ligands and counterions surrounding the 1-D structure has been demonstrated both experimentally and theoretically^{4,5,7}; in particular it was shown⁷ that the NH_3 and Br ligands are necessary for enabling the Peierls distortion in $PtBrn$. Thus, the behavior of a neutral chain solid under pressure should not necessarily be expected to mimic that of charged chain system. We have therefore measured the dependence on high hydrostatic pressure of ν_1 , its first overtone ν_1^{1o} , and an “off-chain” symmetric stretching mode ν_L of $PtBrn$, up to the theoretical value for P_C . The data indicate that an insulator-to-metal transition for this neutral chain system does not occur, implying that a realistic model of the pressure dependence must at least account for either interchain effects or electron-electron interactions. In fact, when we include the latter in our calculations of the uniaxial stress dependence of ν_1 , the results of which are presented below, we can qualitatively reproduce the experimental data.

Raman experiments were performed using a Spex 1877D triple spectrometer coupled with a 298x1152 CCD array, and an Ar^+ -pumped CW Ti:Sapphire laser (Spectra Physics 3900). The average power of the excitation beam (850 nm) was typically 10 mW, focussed to a spot of about 50 μm diameter. Pressures up to 95 kbar were obtained with a Merrill Basset diamond anvil cell filled with cyclohexane; all high P measurements were

performed at 300K. P was determined from the ruby luminescence¹⁵, assuming a shift of the ruby lines of 0.365 Å/kbar¹⁶. Uncertainties in phonon frequency and cell pressure were 0.5 cm⁻¹ and 0.3 kbar, respectively.

The neutral chains were formed from a reaction of a slight excess of PtBr₂(NH₃)₂ in deionized water with one equivalent of PtBr₄(NH₃)₂ under pressure and high temperature (7-10 psi and 110-120 C). Evaporation of the solution in a 90 C oven yielded bronze crystals. The precursors were synthesized from PtCl₂(NH₃)₂ (Aldrich) via a substitution reaction with two equivalents of AgNO₃, forming Pt(NH₃)₂(NO₃)₂, and then resubstituting with two equivalents KBr, forming PtBr₂(NH₃)₂, which can be oxidized to PtBr₄(NH₃)₂ with Br₂.

The Raman spectra at 1 bar and at higher pressures up to 95 kbar (all at 300K) are shown in Fig. 1. The observed line broadening with P has contributions from both anharmonicity, and nonhydrostatic conditions in the cyclohexane above 40 kbar; the latter, however, should not effect the measured shifts of vibrational frequencies with P . We focus on the P dependence of ν_1 , its first overtone ν_1^{10} , and the symmetric stretching mode ν_L of the equatorial Br atoms perpendicular to the chain. From 1 bar to 30 kbar ν_1 decreases, in agreement with our expectations for a CDW and the recent calculations⁸. However, between 30 and 40 kbar the slope is close to zero, and at higher pressures changes sign, such that above 80 kbar ν_1 exceeds its ambient pressure value. This is qualitatively similar to what was observed for ν_1 under pressure in charged PtBr and PtCl chains⁹⁻¹⁴. The pressure dependence of ν_1 is summarized in Fig. 2. We observe that the slope $d\nu_1/dP$ below 30 kbar is much smaller than what is predicted from the LDA calculations. For instance, at low P the data can be fit with a linear slope of -0.46 cm⁻¹/kbar, which extrapolates to zero at 359 kbar.

The initial soft mode behavior of ν_1 with P is consistent with the template effect⁴, and with the recent calculations⁸. As the chain is squeezed, leading to a smaller Pt-Pt separation, and a preferential compression of the long, weaker Pt²⁺-Br bonds, the curvature of the potential well around each Br atom decreases, with a corresponding decrease of ν_1 . At $P=P_C$ each Br atom is forced to be at the midpoint between the Pt atoms, which now become equivalent to each other (Pt³⁺), the solid is predicted to be a 1-D metal, and the formerly symmetric chain mode vanishes from the Raman spectrum because it is now antisymmetric with respect to inversion symmetry in the unit cell, which has been cut in half. Consequently, this process can be described as a second order phase transition with ν_1 as the order parameter. From Landau's theory¹⁷, it follows that,

$$\nu_1 = A|P - P_C|^{1/2}, \quad (1)$$

where A is a constant. This P dependence is actually followed by some materials exhibiting paraelectric to ferroelectric phase transitions¹⁸. The data from 1 bar to 30 kbar can also be fit quite well to Eq. 1, yielding $P_C=196$

kbar, even though such a fit is strictly valid only near $P=P_C$.

The most puzzling feature of Fig. 2 is the change in slope above 30 kbar. One possible origin is increased hard-core repulsion between the Pt and axial Br atoms as they are forced to move toward each other, causing either alternate metals or halogens to buckle out of the chain, and leading to a planar, rather than linear structure. Additionally, we consider the strengthening of interactions perpendicular to the chains upon compression, an effect not accounted for in Ref. 8. For example, a zig-zag structure of the chain may also be induced by the compression of adjacent equatorial Br ligands, which, at ambient pressure, are already separated by only 3.306 Å, less than twice their Van der Waals radius ($2 \times 1.95 \text{ Å} = 3.90 \text{ Å}$)¹⁹. Instead of moving closer together, these atoms may move parallel to the chain, in opposite directions, pulling the axial Br atoms off the chain, and, perhaps, even stretching their bonds to the Pt atoms. We therefore conjecture that either of the above two effects could cause ν_1 to increase with P as optical phonons typically do in 3-D solids in the absence of phase transitions¹⁶. The importance of 3-D interactions was also revealed by LDA calculations based on PtCl⁸, which simulated a reduction in interchain distance for a fixed Pt-Pt separation, and suggested that an increase in overlap between the orbitals of the off-axis ligands and those of the axial Pt and Cl atoms, would increase E_g . We then expect from the template effect⁴, that this would be associated with an increase in ν_1 .

The P dependence of ν_1 in PtBrn is not typical of all MX solids, however. In PtI, for example, a system with a very weak CDW, ν_1 increases with P from 1 bar to 30 kbar¹⁰, opposite to the low P dependence of ν_1 in PtBrn. Nevertheless, the hardening of ν_1 with P that occurs in PtBrn and charged PtBr and PtCl at high P , when the Peierls distortion is ostensibly diminished, may be consistent with the low P behavior of PtI, which is weakly distorted at only 1 bar.

The appearance of two pressure-induced modes at 177 and 192 cm⁻¹ ($P=53$ kbar, Fig. 1) is suggestive of a change in crystal symmetry with P , yet the threshold pressure for these modes was sample dependent, occurring as low as 17 kbar. These modes therefore do not appear to be correlated with the transition at 35 ± 5 kbar, which showed little dependence on sample. However, modes were observed in charged PtBr at 174 and 182 cm⁻¹ with 2.41 eV excitation, and attributed to polaronic defects, the Raman intensities of which were presumably enhanced by optical transitions from the upper halide (X) band to a gap state between the metal (M) bands²⁰. In the mixed-halide compound PtCl _{x} Br _{$1-x$} ($x=0.75$), modes were also observed upon photolysis at 2.54 eV at 171 and 181 cm⁻¹, and ascribed to the symmetric stretching of the axial Br atoms around Pt⁴⁺ on short chain segments²¹. The observation of new modes in this study only at the highest pressures, for fixed excitation energy (1.46 eV), is suggestive of redshifts of the

interband transition energies with pressure, such as the decrease of E_g with P in a PtCl compound¹¹. Thus, for example, resonance with the defect modes may occur only when pressure reduces the separation in energy between the upper X band and the lower M band such that the X to polaron level transition energy approaches E_{ex} . Alternatively, pressure may lead to a reduction of E_g of the short chain segments, which have optical gaps greater than that of the “infinite chain”²²; the symmetric stretching mode for these segments is then enhanced when $E_g \approx E_{ex}$.

Although the structural distortions mentioned above are possible impediments to metallization, we must also consider that pressure forces the CDW to undergo a transition to a different broken-symmetry ground state. We have tried to account for this effect by calculating the band structure for PtBrn within a 2-band, 3/4-filled tight-binding Peierls-Hubbard (PH) model²³ with linear electron-phonon couplings and springs using the Hamiltonian,

$$\begin{aligned}
H = \sum_{i,\sigma} & \left[(-t_0 + \alpha\delta_i)(c_{i,\sigma}^\dagger c_{i+1,\sigma} + c_{i+1,\sigma}^\dagger c_{i,\sigma}) \right. \\
& \left. + (e_i - \beta_i(\delta_i + \delta_{i-1}))n_{i,\sigma} \right] \\
& + \sum_i U_i n_{i,\uparrow} n_{i,\downarrow} \\
& + \sum_i \left[\frac{1}{2} M_i \dot{v}_i^2 + \frac{1}{2} K_{MX} (\delta_i - a_0)^2 \right. \\
& \quad \left. + \frac{1}{2} \kappa_i (\delta_i + \delta_{i-1} - 2a_0)^2 \right. \\
& \quad \left. + P A_\perp (\delta_i - a) \right] \quad (2)
\end{aligned}$$

with nearest-neighbor hopping t_0 , on-site energy (e_i , $e_M = -e_X = e_0 > 0$), on-site (β) and intersite (α) electron-phonon coupling to the deviation δ_i at site i from the reference ($P=0$) lattice constant a_0 , an on-site (U) Hubbard term, effective near-neighbor (K) and next-nearest-neighbor (κ) springs (to model interactions not explicitly included), and pressure P . β may also effectively be viewed as modeling the distance dependence of the Coulomb interaction²⁴. The lattice distortion is determined self-consistently. This implies that with pressure, δ_i acquires an i -independent component, $d_0(P) = \sum_i \delta_i / N < 0$, corresponding to a reduction in the lattice constant, $a^{eff}(P) = a_0 + d_0(P)$, and an increase in the effective hopping integral, $t_0^{eff}(P) = t_0 - \alpha d_0(P)$.

Thus far, we have studied only uniaxial pressure (fixed perpendicular cross-sectional area A_\perp), and ignored interchain interactions, which could give rise to a neutral-ionic transition similar to the case in mixed stack charge-transfer materials¹⁴. For large deviations from the ground state geometry, nonlinear electron-phonon couplings and springs should also be taken into account. The agreement is, however, surprisingly good even with-

out such corrections²⁵. Our modeling indicates that electron-electron correlations and interchain interactions are relatively weak in PtBrn, and thus treatment of the single chain Peierls-Hubbard Hamiltonian within mean field approximation should be valid for PtBrn parameters, though more accurate treatment may be necessary in the high- P regime, in which the lattice distortion may vanish, and interchain interactions become increasingly important.

Using the $P=0$ LDA results⁷ for the band structure and our experimental results, we have determined a parameter set for Eq. 2 that correctly reproduces the low P dependence of ν_1 , as shown in Fig. 2. With these parameters we predict an initial reduction in the amplitude of the CDW lattice distortion, followed by a transition to a pure SDW phase²⁶ near 40 kbar that gives rise to a turnaround in $d\nu_1/dP$, in agreement with our observations, but in contrast to LDA calculations for $P > 0$ ⁸. However, we expect, for negligible spin-phonon interactions, that ν_1 would become Raman inactive in the SDW phase. We are therefore investigating other parameter sets that lead to a transition to a commensurate spin-Peierls phase²⁷, in which ν_1 would remain symmetry allowed.

We find that the first overtone of ν_1 provides further evidence of a pressure-induced phase transition. In Fig. 3 we plot the deviation (from harmonicity), defined as $\Delta\nu = \frac{1}{2}\nu_1^{1o} - \nu_1$, as a function of P . $\Delta\nu$ is positive for almost all P , and exhibits a peak at 35 kbar, which is in the region where ν_1 vs. P is flat. For isolated molecules, overtones are ordinarily at lower frequencies than integral multiples of the fundamental due to anharmonicity²⁸. However, for solids, the first overtone has only to satisfy the sum rule $\vec{q}_1 + \vec{q}_2 \approx 0$, where q_i is the wavevector of each emitted phonon. This implies that the overtone can have contributions from phonons throughout the Brillouin zone, and not just at $q=0$. Since the dispersion curve on which ν_1 lies slopes upwards from $q=0$ to $q = \pi/a_0$ ²⁹, it is plausible that the high frequency of the overtone is due to phonons at $q > 0$. The most likely candidates have wavevectors corresponding to a high density of states $g(q)$. Since $g(q) \sim |\partial\omega/\partial q|^{-1}$ in 1-D, where ω is the angular phonon frequency, the greatest contributions would correspond to extrema of the dispersion curve, such as at $q = 0$ and $q = \pi/a_0$ at ambient pressure. However, as P increases, a kink may develop in the phonon dispersion curve between zone center and zone boundary, giving a high density of states in that region. Such an anomaly was observed via neutron scattering for a soft phonon mode in SrTiO₃ as a function of temperature³⁰. In our case, the kink would probably be correlated with either a change in crystal structure, or a transition from the CDW to another broken symmetry ground state.

We have also investigated the P dependence of another mode ν_L , which has a frequency at 1 bar of 204 cm⁻¹, close to that (207 cm⁻¹) of the Pt-Br vibration of the isolated (Pt²⁺) molecule³¹, and, relative to ν_1 , is

enhanced by light polarized perpendicular to the chains. We therefore attribute ν_L to the symmetric stretch of the equatorial Br atoms around each Pt. As Fig. 2 shows, ν_L increases linearly ($0.37 \text{ cm}^{-1}/\text{kbar}$) up to 95 kbar; this positive slope is in stark contrast to the softening of the chain mode ν_1 at low pressures, and suggests that a CDW does not exist parallel to the equatorial Br ligands. Initially, we had hoped that compression would lead to delocalization along the axis defined by the Pt–equatorial Br atom bonds, and that a CDW would form as a result. This would be facilitated by the close proximity of adjacent equatorial Br atoms to each other, but would require chain-to-chain ordering, manifested as an alternation in the Pt valences. However, the increase in ν_L with pressure is consistent with either a lack of ordering, or, as in our interpretation of the high pressure dependence of ν_1 , a 3-D distortion of the equatorial Br ligands occurs as we attempt to press them together.

In conclusion, we have shown that the pressure dependence of the Raman active chain mode in $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$ at low P is in qualitative agreement with the template effect, and with the theoretical predictions for the quenching of the CDW. At higher P , however, metallization is obstructed by what may be a 3-D distortion of the chains, or a transition to another broken-symmetry state such as a spin-Peierls phase, driven by electron-electron interactions. We believe the present results, in conjunction with those for charged chains, are suggestive of a basic universality in the high pressure response of MX solids. Identification of the origin of this phenomenon may require high pressure X-ray diffraction and magnetic measurements on these materials.

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FIG. 1. Raman spectra excited at 850 nm at various pressures from 1 bar to 95 kbar at 300 K.

FIG. 2. Pressure dependence at 300K of the Raman-active chain mode ν_1 (solid circles), and ν_L (hollow circles), the symmetric stretching mode of the equatorial Br ligands. The solid line through ν_L is a linear fit (see text). The solid line through ν_1 is a theoretical fit based on Eq. 2 using the parameters $t_0=0.98$ eV, $e_0=0.69$ eV, $\alpha=1.56$ eV/Å, $\beta_M=1.37$ eV/Å, $\beta_X=-4.10$ eV/Å, $U_M=1.60$ eV, $U_X=0.32$ eV, $K_{MX}=6.14$ eV/Å² and $K_{MM}=0.61$ eV/Å².

FIG. 3. Pressure dependence of $\Delta\nu$. The solid horizontal line represents $\Delta\nu = 0$, corresponding to a purely harmonic crystal with no density of states effect.