

Pressure tuning of the charge-density wave in the halogen-bridged transition-metal solid $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$

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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 $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$. 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.

The halogen-bridged ($X=\text{Cl},\text{Br},\text{I}$) transition-metal ($M=\text{Pt},\text{Pd},\text{Ni}$) compounds (MX solids) have recently attracted a great deal of attention as paradigms of one-dimensional (1D) systems.¹ 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 1D analogs of high-temperature Cu-O superconductors.³

An MX complex is typically represented by $[\text{ML}_4][\text{MX}_2\text{L}_4]\text{Y}_4$, where L is a ligand molecule, such as ethylamine, X is 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} As a result, 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); the tunability of E_g is a critical property of materials used in optical devices, such as light-emitting diodes.⁶

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 $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$ (abbreviated PtBrn), an MX solid with neutral chains, and, hence, a relatively small number of atoms per unit cell (see Fig. 1 of Ref. 7). This complex 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. The calculation 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 experiments indicated that 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 1D 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 a charged-chain system. We have therefore measured the dependence on high hydrostatic pressure of ν_1 , its first overtone ν_1^{10} , 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 P dependence must at least account for either interchain 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 298×1152 charge-coupled-device array, and an Ar^+ -pumped cw Ti:sapphire laser at 850 nm. The average power of excitation was typically 10 mW, focused 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 300 K. P was determined from ruby luminescence,¹⁵ assuming a shift of the ruby lines of 0.365 $\text{\AA}/\text{kbar}$.¹⁶ Uncertainties in phonon frequency and cell pressure were 0.5 cm^{-1} and 0.3 kbar, respectively.

The Raman spectra at 1 bar and at higher P up to 95 kbar are shown in Fig. 1. The line broadening with P has contributions from both anharmonicity and nonhydrostatic conditions in cyclohexane above 40 kbar; the latter, however, should not affect the measured shifts of vibrational frequencies with P . From 1 bar to 30 kbar ν_1 decreases, in agreement with our expectations for a CDW and Ref. 8. However,

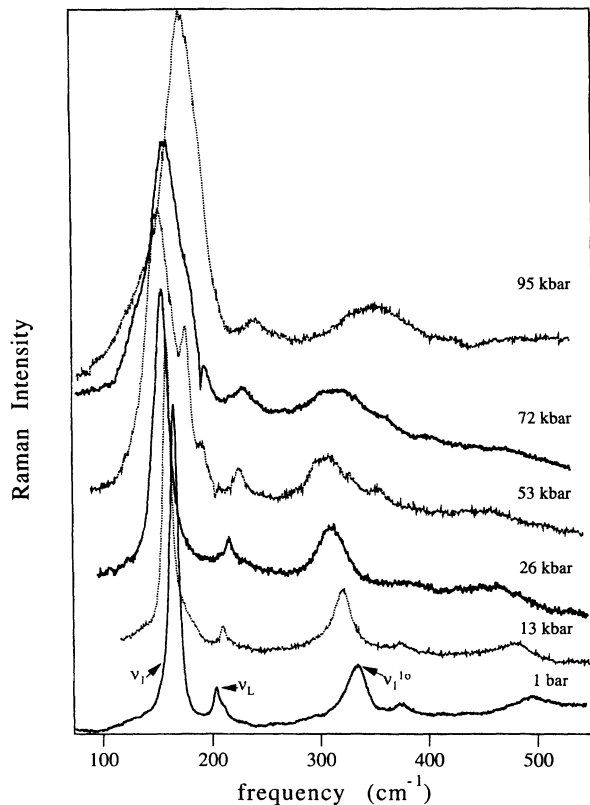


FIG. 1. Raman spectra excited at 850 nm at various pressures from 1 bar to 95 kbar at 300 K.

between 30 and 40 kbar the slope is close to zero, and at higher P 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 chains.^{9–14} The P dependence of ν_1 is summarized in Fig. 2. We observe that $d\nu_1/dP$ 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 $-0.46 \text{ cm}^{-1}/\text{kbar}$, which extrapolates to zero at 359 kbar.

The initial soft-mode behavior of ν_1 with P is consistent with the template effect⁴ and recent calculations.⁸ As the chain is squeezed, leading to a smaller Pt-Pt separation, and a preferential compression of the long, weaker Pt^{2+} -Br bonds, the curvature of the potential well around each axial Br atom decreases, with a corresponding reduction 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 (Pt^{3+}), the solid is predicted to be a 1D metal, and the formerly symmetric chain mode vanishes from the Raman spectrum due to antisymmetry with respect to inversion in the unit cell, which has been halved. Consequently, this process can be described as a second-order phase transition with order parameter ν_1 . From Landau's theory,¹⁷ we have

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

where A is a constant. This P dependence is followed by some materials undergoing paraelectric-to-ferroelectric phase transitions.¹⁸ The data from 1 bar to 30 kbar can also be fit

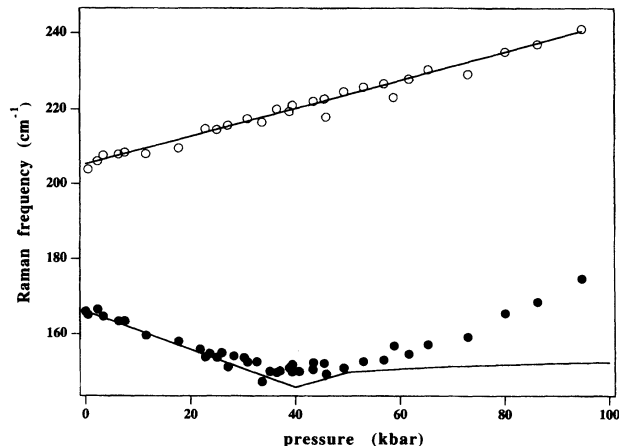


FIG. 2. Pressure dependence at 300 K of the Raman-active chain mode ν_1 (solid circles), and ν_L (hollow circles), the symmetric stretching mode of the equatorial Br ligands. The solid line through ν_L is a linear fit (see text). The solid line through ν_1 is a theoretical fit based on Eq. (2) using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

well to Eq. (1), yielding $P_c = 196 \text{ kbar}$, 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 zigzag structure of the chain may also be induced by the compression of adjacent equatorial Br atoms, which, at ambient pressure, are already separated by only 3.306 \AA , less than twice their van der Waals radius ($2 \times 1.95 \text{ \AA} = 3.90 \text{ \AA}$).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 effects could cause ν_1 to increase with P as optical phonons typically do in 3D solids in the absence of phase transitions.¹⁶ The importance of 3D interactions was also revealed by LDA calculations based on PtCl,⁸ 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 kbar,¹⁰ 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) bands.²⁰ In $\text{PtCl}_x\text{Br}_{1-x}$ ($x=0.75$), modes were also observed upon photolysis at 2.54 eV at 171 and 181 cm^{-1} , and ascribed to symmetric stretching of the axial Br atoms around Pt^{4+} on short chain segments.²¹ The observation of different modes in this paper only at the highest pressures, for fixed excitation energy E_{ex} (1.46 eV), is suggestive of redshifts of the interband transition energies with P , such as the decrease of E_g with P in a PtCl compound.¹¹ Thus, for example, resonance with the defect modes may occur only when pressure reduces the separation in energy between the upper- X and the lower- M bands such that the X -to-polaron-level transition energy approaches E_{ex} . Alternatively, pressure may reduce 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 $E_g \approx E_{\text{ex}}$.

Although the structural distortions postulated may impede metallization, we also consider that pressure induces a transition from the CDW to a different broken-symmetry state. We have tried to account for this by calculating the band structure for PtBrn within a two-band, $\frac{3}{4}$ -filled tight-binding Peierls-Hubbard (PH) model²³ with linear electron-phonon couplings and springs using the Hamiltonian,

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

with nearest-neighbor hopping t_0 , on-site energy ($e_i, e_M = -e_X = e_0 \geq 0$), 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 interaction.²⁴ 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 $a_{\text{eff}}(P) = a_0 + d_0(P)$, and an increase in the effective hopping integral $t_0^{\text{eff}}(P) = t_0 - \alpha d_0(P)$.

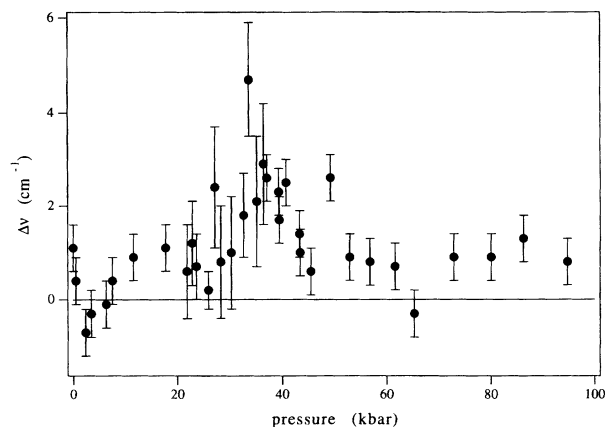


FIG. 3. Pressure dependence of $\Delta\nu$. The solid horizontal line represents $\Delta\nu=0$, corresponding to a purely harmonic crystal with no density-of-states effect.

Thus far, we have studied only uniaxial pressure (fixed perpendicular cross-sectional area A_\perp), and ignored inter-chain interactions, which could give rise to a neutral-ionic transition similar to the case in mixed-stack charge-transfer materials.¹⁴ 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 without such corrections.²⁵ Our modeling indicates that electron-electron correlations and inter-chain interactions are relatively weak in PtBrn, and thus treatment of the single-chain PH 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 phase,²⁷ 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. Figure 3 shows the deviation (from harmonicity), $\Delta\nu = \frac{1}{2}\nu_1^{10} - \nu_1$ vs P . $\Delta\nu > 0$ for almost all P , and peaks 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 anharmonicity.²⁸ However, for solids, the first overtone has only to satisfy $\mathbf{q}_1 + \mathbf{q}_2 \approx \mathbf{0}$, where q_i is the wave vector of each emitted phonon. Thus 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 π/a_0 ,²⁹ it is plausible that the high frequency of ν_1^{10} is due to phonons at

$q > 0$, especially ones with wave vectors corresponding to high densities of states $g(q)$. Since $g(q) \sim |\partial\omega/\partial q|^{-1}$ in 1D, where ω is the angular phonon frequency, the greatest contributions would correspond to extrema of the dispersion curve, such as at $q=0$ and π/a_0 at ambient pressure. However, as P increases, a kink may develop in the dispersion curve between zone center and zone boundary, giving a high $g(q)$ in that region. Such an anomaly was observed via neutron scattering for a soft phonon mode in SrTiO_3 as a function of temperature.³⁰ 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 studied the P dependence of the 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 (Pt^{2+}) molecule,³¹ 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 P , suggesting that a CDW does not exist perpendicular to the chains. Initially, we had hoped that compression would cause delocalization along the Pt-equatorial Br 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 P is consistent with either a lack of ordering, or, as in our interpretation of the high- P dependence of ν_1 , a 3D distortion of the Pt-equatorial Br bonds occurs as we attempt to press these Br atoms together.

In conclusion, the pressure dependence of the Raman-active chain mode in PtBrn at low P qualitatively agrees with both the template effect and theoretical predictions for quenching of the CDW. At higher P , however, metallization is obstructed by either a 3D 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 that 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- P x-ray diffraction and magnetic measurements on these materials.

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²⁶When 3D couplings and corrections to the mean field are added, whether this SDW phase is antiferromagnetic, an actual SDW, or an antiferromagnetic plus CDW spin-Peierls phase (distinct from the MXP spin-Peierls phase—both types of spin-Peierls phases can occur—see Ref. 27) will depend on both chain lengths and the strengths of the 3D couplings. However, such considerations should not change the qualitative arguments here.

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