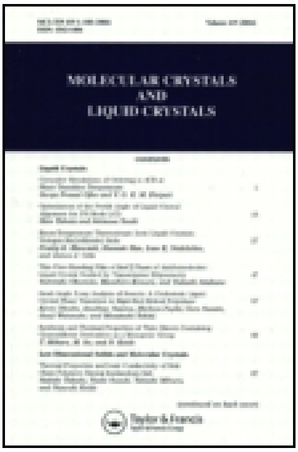

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PRESSURE AND TEMPERATURE INDUCED FREQUENCY SHIFTS OF RAMAN-ACTIVE PHONONS IN THE MX SOLID $Pt_2Br_6(NH_3)_4$

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Abstract We report the dependencies on hydrostatic pressure up to 100 kbar, and on temperature from 10 K to 300 K of the frequencies of Raman-active stretching modes in the single crystal MX chain solid $Pt_2Br_6(NH_3)_4$ (PtBrn). The data show that a predicted pressure-induced metallization does not occur, and suggests instead that either a 3-D structural distortion or a transition to a broken-symmetry ground state different from the charge-density wave (CDW) takes place.

INTRODUCTION

The halogen-bridged (X=Cl,Br,I) transition metal (M=Pt,Pd,Ni) compounds (MX solids) are attracting a great deal of attention as paradigms of 1-D systems.[1] One recently discovered phenomenon in these materials, known as the template effect, is the influence of ligands and counterions on the distance d between adjacent M atoms along the chain.[2,3] We have observed[3] that both the frequency of the Raman-active chain mode ν_1, and the energy gap E_g, increase as d increases. This tunability of E_g is clearly a desirable feature in materials used in optical devices, such as light-emitting diodes.[4]

Alouani et al.[5] predicted that applying uniaxial stress along the chain axis in $Pt_2Br_6(NH_3)_4$ (PtBrn), an MX solid with the smallest number of atoms per unit cell, would lead to metallization (equal distances between all axial Br and Pt atoms) at 89 kbar. ν_1 would then vanish as the stretching mode became asymmetric (and, therefore, Raman inactive) with respect to the new (two atom) unit cell of the chain. We present here our high pressure Raman studies of PtBrn which were undertaken to test this prediction.

EXPERIMENT

Raman experiments were performed using a Spex 1877D triple spectrometer coupled with a 298x1152 CCD array. Pressures were obtained using a diamond anvil cell (DAC) filled with cyclohexane; for calibration we used the ruby fluorescence method,[6] assuming a shift of the ruby lines of 0.365 Å/kbar.[7] All high pressure measurements were performed at room temperature with excitation between 1.30 eV (950 nm) and 1.46 eV (850 nm).

RESULTS AND DISCUSSION

Raman results for PtBrn at ambient pressure were first presented by Clark et al.,[8] who identified as ν_1 an intense line near 165 cm^{-1}, strongly polarized parallel to the chains. The pressure (P) dependence of this mode is shown in Fig. 1. From 0 to 30 kbar the frequency decreases, in agreement with the theory.[5] 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 behavior is qualitatively similar to what was observed for ν_1 under pressure in charged PtBr and PtCl chains.[9-13] Since ν_1 does not decrease to zero, it appears that metallization does not occur, although linear extrapolation of the data (slope = -0.46 cm^{-1}/kbar below 30 kbar), gives a zero frequency intercept at 359 kbar.

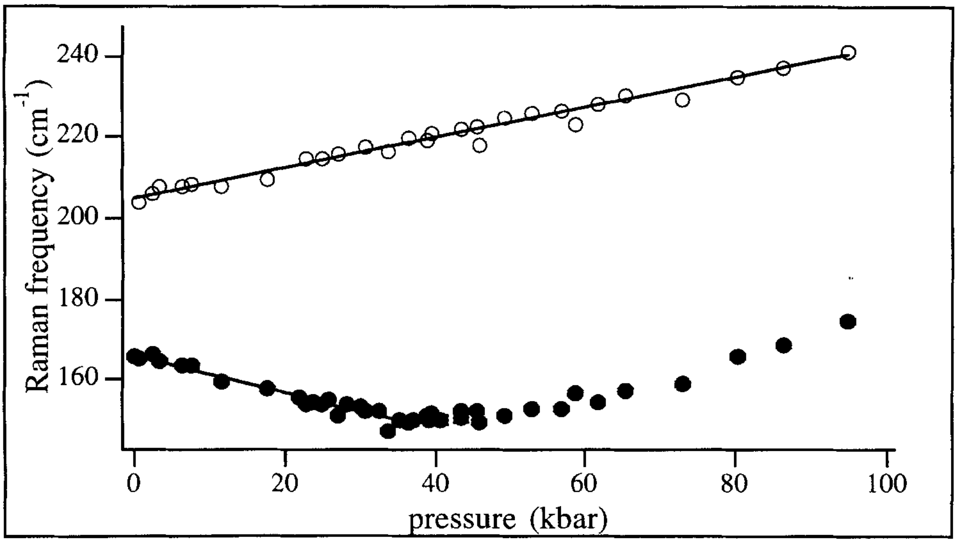

FIGURE 1 Pressure dependence of ν_1 (solid circles), and ν_L (hollow circles). The solid lines are linear fits.

We consider an increase in dimensionality as the most likely explanation for the data above 30 kbar. This may be caused by an increase in hard-core repulsion between the Pt and axial Br atoms as the crystal is compressed, forcing alternate metals or halogens to buckle out of the chain. Another mechanism could be the strengthening of interactions perpendicular to the chains upon compression of adjacent equatorial Br ligands, which, at 1 bar, are separated by less than twice their Van der Waals radius. Instead of moving closer together, these atoms may move parallel to the chain, in opposite directions, pulling the Pt atoms off axis. In either case, the increase in dimensionality could render a Peierls distortion energetically unfavorable, causing ν_1 to increase with pressure as optical phonons typically do in 3-D solids in the absence of phase transitions.[7]

We also studied the pressure dependence of the frequency of the symmetric stretching mode (ν_L) of the equatorial Br ligands (parallel to the b-axis), which has a frequency at 1 bar of 207 cm^{-1}, the same as that for the isolated molecule.[14] Fig. 1 shows that ν_L increases linearly (0.37 cm^{-1}/kbar) up to 94 kbar; this positive slope is in stark contrast to the softening of ν_1 at low pressures. One might expect that applying pressure could cause a CDW to form along the b-axis if there were chain-to-chain ordering, manifested as an alternation in the Pt valences. However, the increase in ν_L with pressure suggests that either there is no ordering, or, as in our interpretation of the high pressure dependence of ν_1, that a 3-D distortion of the equatorial Br ligands occurs as we attempt to press them together.

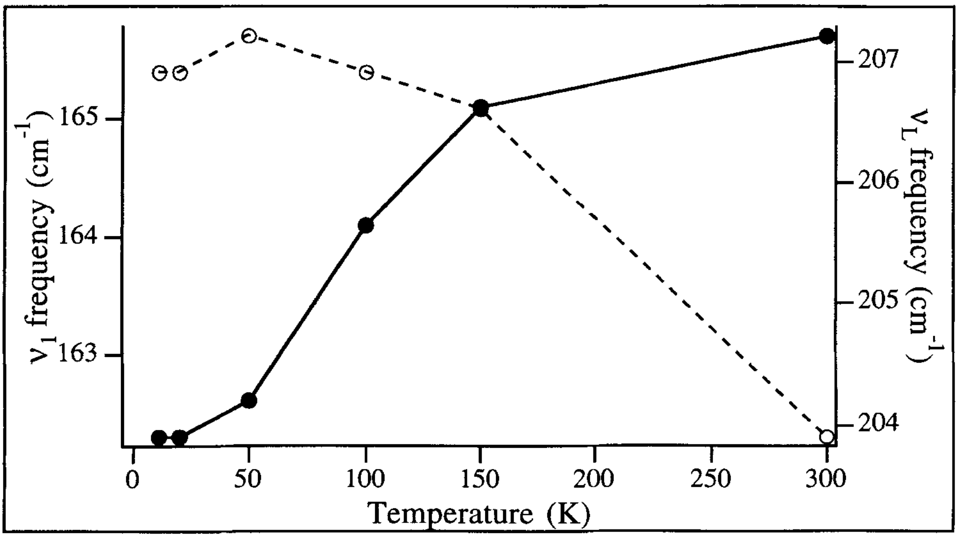

FIGURE 2 Temperature dependence of ν_1 (solid line through solid circles), and ν_L (dashed line through hollow circles) at 1 bar.

The temperature (T) dependence of ν_1 is shown in Fig. 2. Again, we see a dramatic difference between the behaviors of ν_1 and ν_L. The relation between these data and those in Fig. 1 is[7]

$$\frac{d\nu_i}{dT} = \left(\frac{\partial \nu_i}{\partial T}\right)_V - \left(\frac{\alpha}{\beta}\right)\left(\frac{\partial \nu_i}{\partial P}\right)_T , \qquad (1)$$

where ν_i is the frequency of normal mode i, V the volume, α the coefficient of thermal expansion, and β the compressibility. The first (explicit) term, which assumes constant atomic equilibrium spacing, is associated with thermally-induced changes in the phonon occupation numbers $n_j(T)$ of the other normal modes $j \neq i$ of the crystal. Interactions among modes lead to a decrease in frequency relative to that at absolute zero given by[15]

$$\nu_i(T) = \nu_i(0) - \sum_j B_j n_j(T), \qquad (2)$$

where B_j is a function of the phonon frequencies and anharmonicity constants. The second (implicit) term in Eq. (1), on the other hand, corresponds to changes in frequency due to expansion of the crystal. From Figs. 1 and 2 we have determined that the implicit term is the dominant one for both ν_1 and ν_L. The increase in ν_1 with T for an MX solid is consistent with the template effect since thermal expansion would increase d, thereby having the opposite effect of pressure.

CONCLUSIONS

We have shown that the pressure dependence of ν_1 in $Pt_2Br_6(NH_3)_4$ at low pressures is consistent with the template effect, and with the theoretical predictions for the quenching of the CDW. At higher pressures, however, metallization is obstructed by what may be a 3-D distortion of the chains, although we cannot yet rule out the possibility that the change in sign of $\left(\frac{\partial \nu_1}{\partial P}\right)_T$ is associated with a transition to another broken-symmetry state such as a spin-Peierls phase.[16]

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