PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 58, NUMBER 5 1 AUGUST 1998-I

BRIEF REPORTS

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Raman-scattering study of phase transitions in methylmercury(II) halides $CH_3HgX (X=Cl,Br,I)$

D. Kirin*

Ruder Bošković Institute, POB 1016, 10001 Zagreb, Croatia

(Received 1 December 1997; revised manuscript received 18 February 1998)

The phase transition in methylmercury(II) halides $CH_3HgX,(X=Cl,Br,I)$ has been studied using Raman spectroscopy in the temperature range from 10 to 390 K. A soft mode was observed in all studied compounds. The low-frequency Raman spectra of all methylmercury(II) halides (MMH) show several common features. On these grounds and available structural data we conclude that all methylmercury(II) halides are isostructural, with a high-temperature tetragonal phase and a low-temperature orthorhombic one. The possible mechanism of the phase transition is described. The transition is ferroelastic, driven by the softening of a phonon at the Brillouin zone boundary. We assume that the transition is induced by the freezing of the eigenvector of a zone boundary transversal acoustic phonon, causing the cell doubling in the low-temperature phase. [S0163-1829(98)08529-4]

I. INTRODUCTION

Structural phase transitions in solids have been extensively studied both experimentally and theoretically over the past decades.[1,2] The most studied type of structural phase transition is the displacive phase transition, associated with a small displacement of atoms from the equilibrium position, which cause a change of crystal symmetry. Raman spectroscopy is particularly suitable for the study of this type of transition, since a change of the symmetry associated with the phase transition affects the Raman spectroscopy selection rules, and different phases are characterized by different spectra.[3] A change of symmetry is usually a consequence of the freezing of a soft mode, i.e., a mode whose frequency decreases to zero on approaching the temperature of the phase transition.

In molecular solids there are relatively few examples of displacive phase transitions, and biphenyl[4] and chloranil[5] are the most studied and best understood examples.

A sequence of phase transitions in CH_3HgCl and CH_3HgBr crystals was observed using Raman spectroscopy and the transitions were associated with a well pronounced temperature- and pressure-dependent soft mode.[6] At zero pressure, the temperature of the phase transition was found to be 162 K for the CH_3HgCl crystal and 310 K for the CH_3HgBr one.[6] The authors of Ref. 6 concluded that there was no phase transition in CH_3HgI and that its crystal structure was different from the structure of chlorine and bromine.

Solid state properties of methylmercury(II) halides $CH_3HgX(X=Cl,Br,I)$ have not been yet extensively studied. The aim of the present work is therefore to study the observed phase transitions in the broadest possible temperature range (from 10 K to the vicinity of the melting temperature), in order to elucidate the mechanism of the phase transition.

II. EXPERIMENT

The low-frequency Raman spectra of CH_3HgCl and CH_3HgBr crystals were recorded in the temperature range from 10 to 330 K, and the Raman spectra of CH_3HgI were recorded in the temperature range from 10 to 390 K. The spectra were recorded using a DILOR Z 24 single-channel instrument and a Coherent Innova 100-15 argon ion laser. The low-temperature environment was produced by a CRI Lake Shore closed cycle helium cryostat. The polycrystalline sample was enclosed in a sealed glass capillary mounted on a custom-made brass holder attached to the cryostat. Although the powder sample was used, it was possible to record the low-frequency Raman spectra down to 5 cm^{-1},

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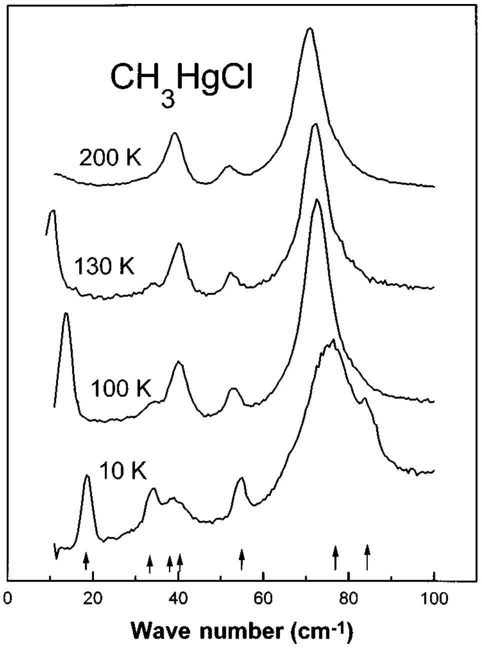

FIG. 1. Low-frequency Raman spectra of CH_3HgCl in the temperature range 10–200 K.

owing to the excellent suppression of elastically scattered laser light.

III. RESULTS

The low-frequency Raman spectra of MMH crystals at different temperatures are shown in Figs. 1–3. The observed spectra of all MMH crystals studied show several common features.

The first feature, found in the low-frequency Raman spectra of *all* studied MMH crystals, is the existence of a well-pronounced soft mode (Fig. 4). An interesting feature observed in the present study is the existence of a soft mode in the CH_3HgI crystal too. We have not been able to determine the temperature of the phase transition. More precisely, it is not clear if the CH_3HgI crystal first melts ($T_m = 416$ K) or undergoes a phase transformation to the high-temperature phase before melting. The existence of a soft mode is usually a sign of a phase transition.

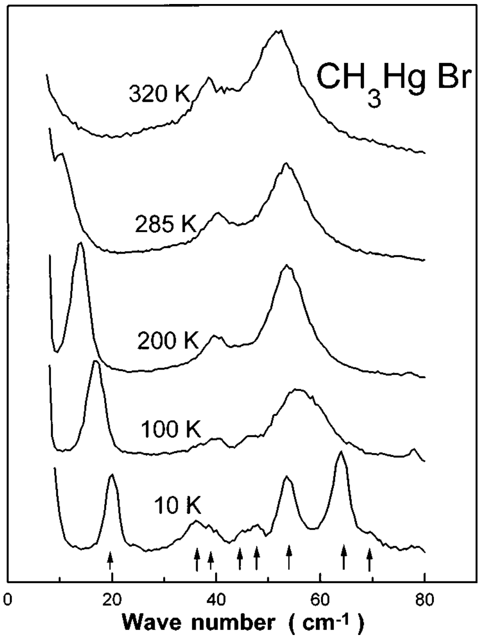

FIG. 2. Low-frequency Raman spectra of CH_3HgBr in the temperature range 10–320 K.

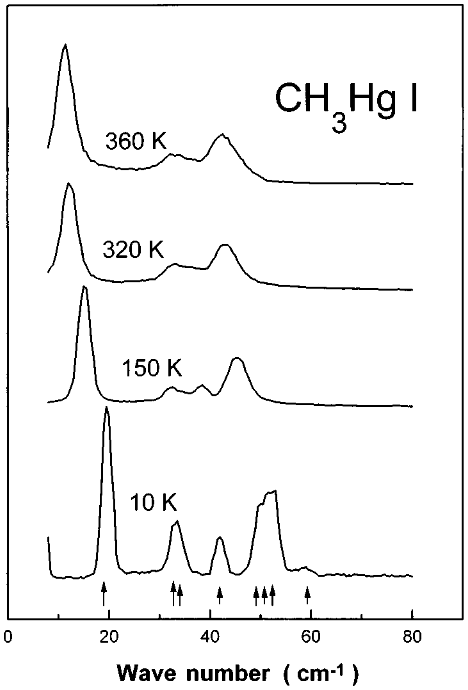

FIG. 3. Low-frequency Raman spectra of CH_3HgI in the temperature range 10–360 K.

The second common feature is the similarity between the low-frequency Raman spectra of different MMH, particularly at the temperatures close to the phase transition temperature T_c.

The third common feature is the fact that the low-frequency Raman spectra of all systems show nearly the same number of lines in the low-temperature phase far from the transition. At the lowest experimental temperature (10 K), seven Raman lines are observed in the low-frequency spectra of CH_3HgCl and eight lines in the spectra of

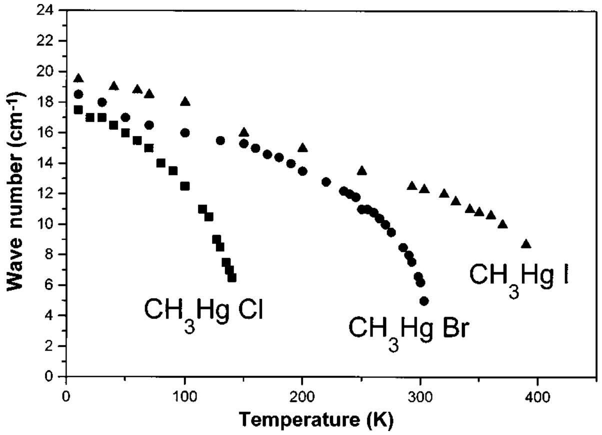

FIG. 4. Temperature dependence of the soft mode in MMH crystals.

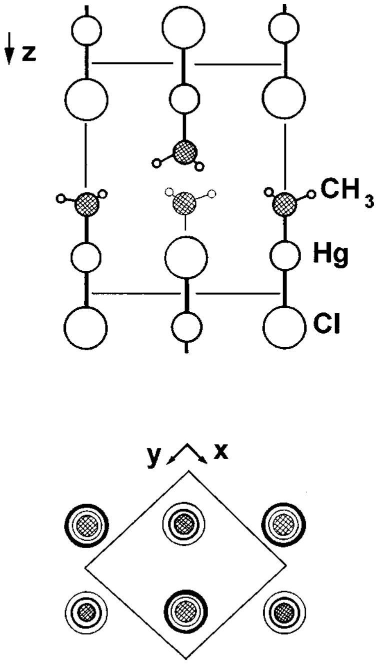

FIG. 5. The room-temperature structure of CH_3HgCl crystal.

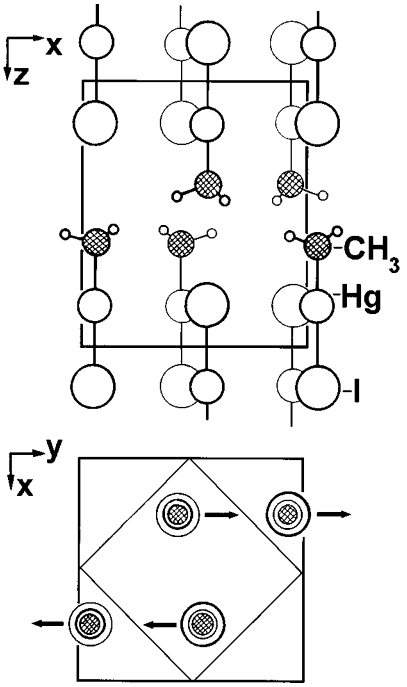

FIG. 6. The room-temperature structure of CH_3HgI crystal. The proposed eigenvector of the Raman active soft mode is shown by the arrows.

CH_3HgBr and CH_3HgI. The observed Raman bands at 10 K are shown by the arrows in Figs. 1–3. The basic obstacle in understanding the mechanism of the phase transition is lack of accurate structural data. A structural study of MMH crystals was made by Grdenić and Kitaigorodsky, who determined the room-temperature structure of CH_3HgCl as tetragonal,[7] the space group $P4/nmm$. The structural results of Kotur *et al.*[8] showed that at room temperature CH_3HgI crystallized in the orthorhombic system, the space group $Pmab$ ($Pbcm$ in standard notation) (Fig. 6). The structural data for CH_3HgBr at room temperature are still controversial. This is probably due to the fact that the phase transition temperature is close to room temperature ($T_c=310$ K), making the determination of the crystal structure difficult. The room-temperature structure of MMT crystals is characterized by layers of molecules in the crystal *ab* plane in both, the tetragonal phase[7] CH_3HgCl (Fig. 5) and the orthorhombic phase[8] CH_3HgI (Fig. 6).

IV. DISCUSSION AND CONCLUSION

In the present study we considerably extended the temperature range in which the low-frequency Raman spectra have been measured so far. On the grounds of the present spectroscopic results and available structural data[7,8] we propose a model for the phase transition in MMH crystals.

Since the present study shows that the low-frequency Raman spectra of MMH crystals have a number of similarities, we propose that all MMH crystals are isostructural. This means that the low-temperature (LT) phase is orthorhombic and the high-temperature (HT) phase is tetragonal. At room temperature CH_3HgBr and CH_3HgI are in the LT orthorhombic phase, while CH_3HgCl is in the HT tetragonal phase.

The similarity between the molecular packing of MMH crystals and another class of relatively well studied mercury compounds $Hg_2X_2(X=\mathrm{Cl,Br})$ (Refs. 10–16) has enabled us to propose a microscopic model of the phase transition in MMH crystals. We propose that the transition is a displacive ferroelastic transition, accompanied by a spontaneous deformation of the crystal lattice in the low-temperature phase. In Hg_2X_2 crystals, the transition is driven by the condensation of a soft acoustic mode at the Brillouin zone boundary of the high-temperature phase. We propose that the phase transition in MMH crystals is also driven by softening of an acoustic mode at the Brillouin zone boundary. The phase transition causes the cell doubling in the LT phase with four molecules in the unit cell, in agreement with a large number of Raman lines observed at low temperatures.

At room temperature CH_3HgI is in the low-temperature orthorhombic phase, the space group[8] $Pmab$ ($Pbcm$) with four molecules in the unit cell (Fig. 6), which is also a probable room-temperature space group of the CH_3HgBr crystal. The number of Raman active modes in the low-temperature orthorhombic phase is given by

$$\Gamma_{\mathrm{LT}}=3A_g+3B_{1g}+2B_{2g}+2B_{3g}.$$

Ten bands should be observed in the low-frequency Raman spectrum, which is close to the number actually observed in the Raman spectra at lowest temperatures (Figs. 1–3) (seven lines in the low-frequency spectrum of CH_3HgCl, eight in CH_3HgBr, and eight in CH_3HgI). Some of the observed lines are probably very close (it is not possible to resolve them even at 10 K); some are very weak lines, and it is difficult to observe them in the polycrystalline sample.

In the high-temperature tetragonal phase there are two molecules in the unit cell. This is the room-temperature structure[7] of CH_3HgCl. In the tetragonal phase the number of Raman active modes is given by

$$\Gamma_{\mathrm{HT}}=A_{1g}+2E_g.$$

Only three modes should be observed in the low-frequency Raman spectrum of the high-temperature phase of MMH crystals ($2E_g$ and A_{1g}), which is in agreement with all the observed spectra and the previous measurements.[17] Three low-frequency Raman bands have been observed in CH_3HgCl at $T>162$ K and in CH_3HgBr at $T>310$ K (Figs. 1 and 2).

For a given HT phase, group theory considerations restrict possible LT space groups for the ferroelastic type of the phase transition.[9] The ferroelastic phase transition between the HT space group $P4/nmm$ and the LT space group $Pmab$ ($Pbcm$) is allowed by symmetry, and is associated with a two-dimensional order parameter. The transition is driven by a phonon instability at the M point on the boundary of the Brillouin zone. (Table VII, p. 1158 of Ref. 9). It means that the MMH crystals are ''improper'' ferroelastics.

The proposed model is also in agreement with the fact that the Raman active soft mode is present only in the spectra of the LT phase. In the HT phase, the soft transverse acoustic mode is at the Brillouin zone boundary (M point), and it is not active in Raman spectra. This mode was observed in the HT phase of Hg_2Cl_2 crystal (X point) using inelastic neutron scattering.[13–15] The doubly degenerate soft mode of the HT phase has two components in the LT phase. They have A_u and A_g symmetry in the LT phase. The Raman active soft mode in the LT orthorhombic phase is a translational mode of the A_g symmetry (Fig. 6) and was also observed in Hg_2Cl_2 and Hg_2Br_2 crystals.[10,12,15,16] The A_u mode is not active in Raman or infrared spectroscopy, i.e., it is a so-called ''silent'' mode.

There are only a few studies of MMH molecules in the crystal phase. There are no measurements of the temperature dependence of the elastic constants, structural data as a function of temperature, or specific-heat measurements.

Besides the structural phase transition, MMH crystals have a number of additional interesting properties. The first is a large splitting of intramolecular vibrations in the crystal, i.e., the splitting between g (Raman active) and u modes (IR active modes). The observed splitting[17] is of the order of 20 cm^{-1}, indicating the strong intermolecular interactions in MMH crystals. The second interesting feature is an unusual temperature dependence of the C-H stretching modes (3000 cm^{-1} region) and the CH_3 group torsional mode (100–200 cm^{-1} region).[18] The changes of the frequencies and intensities of those modes most likely reflect different rotational dynamics of the methyl group at different temperatures. The motion of the methyl group is probably influenced both by the methyl-methyl and methyl-halogen interactions (Figs. 5 and 6). We hope that the future spectroscopic and structural studies at different temperatures will give more complete information about the phase transitions, intermolecular interactions, and methyl group dynamics in this class of molecules.

ACKNOWLEDGMENTS

The author is indebted to Professor J. Mink for providing the samples of CH_3HgBr and CH_3HgI. The unpublished structural results provided by Professor M. Sikirica were valuable in putting forward the mechanism of the phase transition in MMH crystals. The author also thanks Professor Z. Meić for numerous fruitful discussions. This work was supported by the Croatian Ministry of Science and Technology under Contract No. 009803/03.

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*Electronic address: kirin@olimp.irb.hr

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