

## Raman Study of the Phase Transition in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZnCl}_4$ Single Crystals

Tsai-Shia Jung, Hsiang-Lin Liu and Jiang-Tsu Yu  
*Institute of Physics, National Taiwan Normal University,  
Taipei, Taiwan 116, R.O.C.*  
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Polarized Raman spectra of oriented single crystals  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZnCl}_4$  (TEAZ) have been recorded from 320 K to 40 K during both cooling and heating cycles, covering the known phase transitions. The temperature dependence of the internal vibration of the  $\text{ZnCl}_4^{2-}$  ion and C-C bond is explained in terms of the motional narrowing due to the disordering  $\text{CH}_3$  group in TEAZ, which results in the splitting of the  $\text{ZnCl}_4^{2-}$  and C-C lines in the internal mode region. Our Raman data shows that the phase transition is associated with the onset of the  $\text{CH}_3$  group disordering. We have also observed that the phase transition exhibits thermal hysteresis.

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### I. Introduction

First-row transition metal compounds of the form  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{MCl}_4$  (in which M represents Mn, Fe, Co, Ni, Cu or Zn) have attracted much interest due to various structural transformations, related to the dynamics of the organic cations and inorganic anions, which they undergo. For any  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{MCl}_4$ -type crystals, no structural analysis has been performed even at room temperature. It was predicted by Wolthuis *et al.*, on the basis of the measured lattice constants, that the compounds  $\text{MnCl}_4$  and  $\text{ZnCl}_4$  are isostructural with  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{NiCl}_4$  [1]. But the symmetry and structure below the transition temperature has not been determined. It was reported by Melia *et al.*, based on the results of DSC (differential scanning calorimetry) measurements, that there exist two phase transitions at temperatures between 213 K and 218 K in  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZnCl}_4$  during cooling, and one phase transition at 227 K on heating [2]. Up to now, investigations of nuclear magnetic resonance (NMR) and dielectric measurements [1], heat capacity [2, 3], dielectric dispersion [4], EPR spectrum [5, 6] have been reported for these materials. In this paper we present the results of a polarized Raman scattering investigation of a  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZnCl}_4$  single crystal.

### II. Experimental

Single crystals of  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{ZnCl}_4$  (TEAZ: tetraethyl-ammonium tetrachlorozincate) were grown by mixing ethanolic solutions containing stoichiometric amounts of tetraethylammonium chloride and zinc chloride. TEAZ exhibits tetragonal symmetry, the space group is  $\text{P}4_2/\text{nmc}$  with  $Z = 2$ , cell constants are  $a = 9.04 \text{ \AA}$  and  $c = 14.99 \text{ \AA}$  at room temperature [1]. The crystals we

have grown show large hexagonal faces or small square faces (2 mm  $\times$  mm). Using a polarizing microscope, we find that the square faces are (001), and the hexagonal ones are (101) or (110).

The Raman scattering spectra were recorded using a Dilor XY 800 spectrometer with standard attachments. Our light Source was an Ar<sup>+</sup> laser ( $\lambda = 514.5$  nm). The laser power was kept low ( $< 30$  mW) to avoid sample damage. These instruments provided resolutions of about  $1 \text{ cm}^{-1}$ . The experiments were carried out in a  $180^\circ$  scattering configuration. Low-temperature measurements were performed using a closed-cycle helium cryostat system, and the temperature was controlled by a Lakeshore 330 controller.

### III. Results and discussion

According to Torgashev *et al.*, [7], the Raman spectrum of a TEAZ single crystal can be divided into three parts: (1) the external vibration modes below  $100 \text{ cm}^{-1}$ ; (2) the vibrational modes of the  $\text{ZnCl}_4^{2-}$  anion at  $100 \gg 350 \text{ cm}^{-1}$ ; and (3) the vibrational modes of the  $\text{TEA}^+$  cation at above  $350 \text{ cm}^{-1}$ . We will discuss our experimental results according to this classification.

#### III-1. External modes

Figures 1(a) and 1(b) show, respectively, the Raman spectra of the external modes in the (ZZ) polarization on cooling and on heating. On cooling, changes in the spectrum were observed between 220 K and 210 K, while on heating they occurred between 240 K and 250 K. This thermal hysteresis in the external modes agrees very well with other observations [1, 5, 6], and can be taken as a consequence of the occurrence of a phase transition. On cooling, the Raman profiles of the external modes changes abruptly, and no soft modes were observed. These lead us to believe that the phase transition in the TEAZ crystals belongs to the order-disorder type. Concurrent with the onset of this type of phase transition, changes in the profiles of the internal modes are usually observed [8], and this is indeed the case for TEAZ crystals.

#### III-2. Internal modes

##### (a) Vibration of the anions

Figures 2(a) and 2(b) show, respectively, the Raman spectra of the internal modes in the (ZZ) polarization on cooling and on heating. Clearly observable changes in the spectra were recorded at around  $130 \text{ cm}^{-1}$  and  $278 \text{ cm}^{-1}$ . A splitting of the spectrum was observed concurrent with the onset of the phase transition. According to previous reports [7, 9], the peaks at  $130 \text{ cm}^{-1}$  and  $278 \text{ cm}^{-1}$  can be respectively assigned as the  $F_2$  and  $A_1$  vibration modes of the  $\text{ZnCl}_4^{2-}$  anion.

##### (b) Vibration of the cations

Figure 3 shows the spectrum of the cation at  $600 \gg 1200 \text{ cm}^{-1}$  in the (XZ) and (ZZ) polarizations, at room temperature. It can be noted that the  $1183 \text{ cm}^{-1}$  vibration mode, which was observed in the (XZ) polarization, is not observed in the (ZZ) polarization; while the  $1008 \text{ cm}^{-1}$  vibration mode observed in the (ZZ) polarizations is absent in the (XZ) polarization. Figure 4 shows the spectra of the anion in the (XZ) and (ZZ) polarizations, at a temperature below the phase transition. Two additional vibration modes were observed at temperatures below the phase transition. Furthermore, the profiles of the  $900 \text{ cm}^{-1}$  and  $1073 \text{ cm}^{-1}$  peaks exhibit splitting. In Table I, the vibration modes and the symmetries of three compounds containing TEA ion are listed, for those modes with frequencies at around  $900 \text{ cm}^{-1}$  and  $1073 \text{ cm}^{-1}$  [10, 11]. It can be

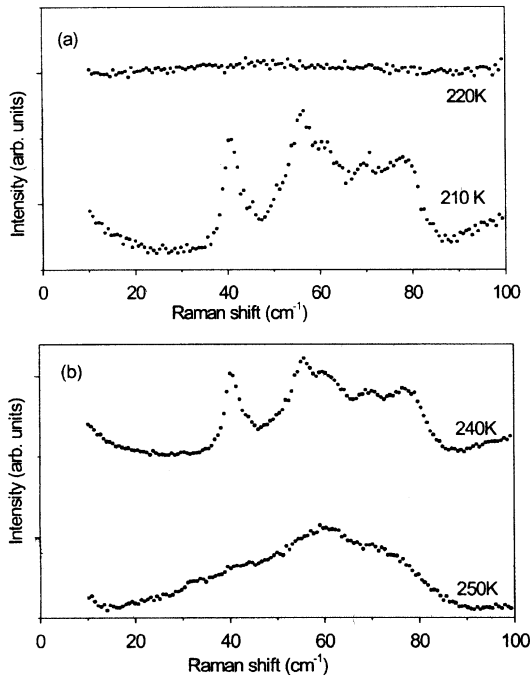


FIG. 1. Temperature dependence of the Raman spectra of the TEAZ crystal in the (ZZ) scattering geometry below  $100 \text{ cm}^{-1}$ . (a) on cooling, (b) on heating.

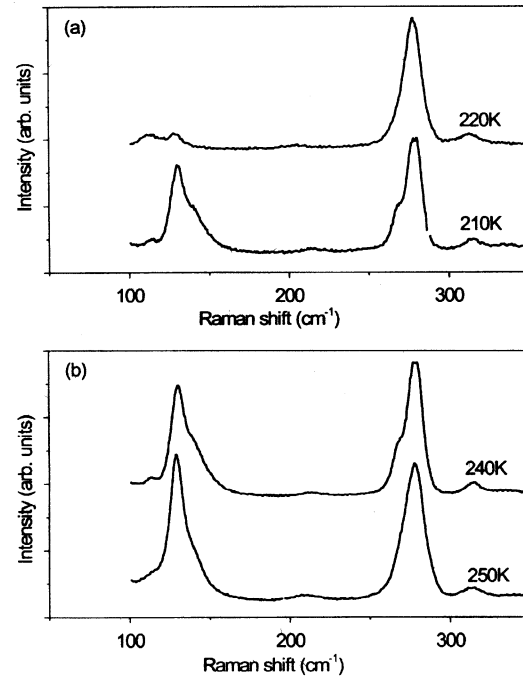


FIG. 2. Temperature dependence of the Raman spectra of the TEAZ crystal in the (ZZ) scattering geometry between  $100 \text{ cm}^{-1} \gg 350 \text{ cm}^{-1}$ . (a) on cooling, (b) on heating.

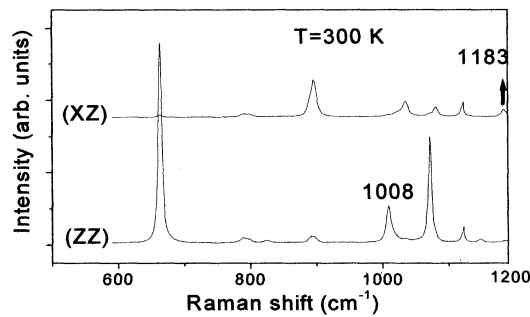


FIG. 3. Raman spectra in the (XZ) and (ZZ) configurations between  $600$  and  $1200 \text{ cm}^{-1}$  at  $300 \text{ K}$ .

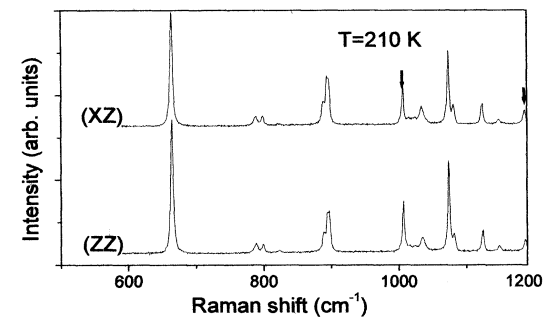


FIG. 4. Raman spectra in the (XZ) and (ZZ) configurations between  $600$  and  $1200 \text{ cm}^{-1}$  at  $210 \text{ K}$ . Two additional modes at  $1008 \text{ cm}^{-1}$  and  $1183 \text{ cm}^{-1}$  were observed.

noted from the data shown in Table I that these two vibration modes observed below the phase transition are the rock modes of the  $\text{CH}_3$  molecule, and that the modes that exhibit splitting belong to the C-C vibration modes.

TABLE I. The vibrational modes and assignments of the Raman bands of the  $N(C_2H_5)_4$ -ion in three compounds.

Mode	$[N(C_2H_5)_4]_2ZnCl_4$ This work	$N(C_2H_5)_4SbF_6$ (Ref. 10)	$[N(C_2H_5)_4]_2HgI_4$ (Ref. 11)	Symmetry Assignment
$\circ_4$	900 $cm^{-1}$	904 $cm^{-1}$	894 $cm^{-1}$	$A_1$ , (C-C)
$\circ_{11}$	1183 $cm^{-1}$	1172 $cm^{-1}$	–	E, (CH <sub>3</sub> -rock)
$\circ_{29}$	1008 $cm^{-1}$	1000 $cm^{-1}$	1000 $cm^{-1}$	$F_2$ , (CH <sub>3</sub> -rock)
$\circ_{31}$	1073 $cm^{-1}$	1068 $cm^{-1}$	1066 $cm^{-1}$	$F_2$ , (C-C)

Wolthuis *et al.* [1] considered the motion of the  $TEA^+$  ion as being comprised of the following four parts: the rotation of the outermost  $CH_3$  molecular groups; the rotation of the  $CH_2$  molecules; the rotation of the whole  $TEA^+$  molecule about its fourfold axis; and the rotation of the whole molecule about all possible orientations. As the time span of interaction between a photon and a molecule is shorter than the period of the molecular flipping, microregions and short-term disorders in molecular arrangements can then be detected in Raman experiments [12]. It is due to this kind of momentary disorder that causes the  $CH_3$  molecular groups to lose its center of symmetry, and makes all of its vibration modes Raman active [13]. The rock modes of the  $CH_3$  molecular groups we have observed in TEAZ in the (XZ) and (ZZ) polarizations can be explained as such. A similar situation has been observed in  $NaNO_2$  as well [14].

The splittings observed in the  $F_2$  and  $A_1$  vibration modes of the  $ZnCl_4^{2-}$  ion and the C-C vibration mode of the  $TEA^+$  ion can be explained by the motional narrowing theory [15]. This theory argues that when the motional velocity of the nearby molecules is smaller than a certain value, a single peak in the NMR spectrum will split. This theory has been successfully used to explain the mode splittings observed in Raman spectra [8, 16]. This splitting occurs because a time-varying field accompanies the molecular motion of the nearby polar molecules. In TEAZ crystals, it is likely that the rotational disorder of the  $CH_3$  molecular groups at temperatures below the phase transition creates a time-varying field for its nearby molecules, which causes the vibration modes of the C-C bond and the  $ZnCl_4^{2-}$  ions to split. Figure 5(a) shows the Raman spectrum of TEAZ crystals in the (XZ) polarization at 300 K; the lower pattern was observed after the crystal had been cycled through the phase transition. Figure 5(b) shows a similar spectrum for the (ZZ) polarization. It can be noted that the splitting of the C-C vibration mode persists at 300 K for sample crystals that have been thermally cycled through the phase transition. This suggests that once a crystal has been cooled to reach its molecular ordered state, it would not immediately return to the disordered state in subsequent heating.

#### IV. Conclusion

The Raman spectra were measured in TEAZ single crystals in the temperature range above and below the transition temperature. It was found that the 278  $cm^{-1}$ , 900  $cm^{-1}$  and 1073  $cm^{-1}$

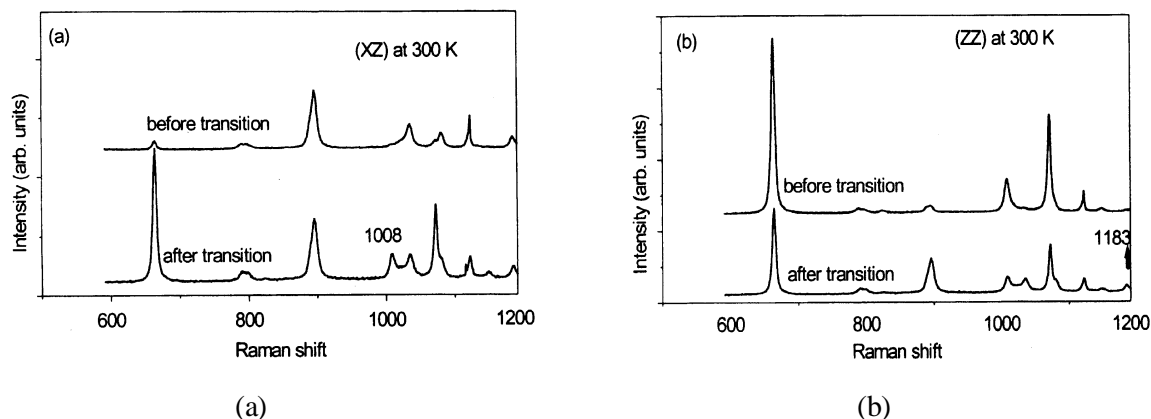


FIG. 5. Raman spectra between 600 and 1200  $\text{cm}^{-1}$  at 300 K before and after transition. (a) in the (XZ) configuration, (b) in the (ZZ) configuration.

bands split as the temperature was decreased to below the transition temperature. This behavior can be understood according to the motional narrowing theory. This may imply that the transition is likely to be triggered by the disordering  $\text{CH}_3$  group on going in TEAZ. We have also observed that the Raman spectra of the crystals exhibiting hysteresis ongoing through the reported phase transition temperature.

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