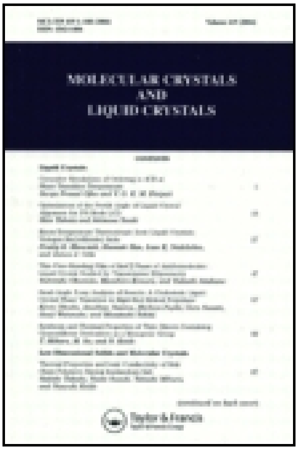

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Optical and Calorimetric Studies on the Role of Lattice Mode Softening for Assisting a Thermally Induced Solid State Reaction

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Optical and Calorimetric Studies on the Role of Lattice Mode Softening for Assisting a Thermally Induced Solid State Reaction

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The concept of phonon assisted solid-state chemical reactions is analyzed in the case of the thermal rearrangement of methyl p-dimethylaminobenzenesulfonate (MSE) to a zwitterionic product p-trimethylammoniumbenzenesulfonate (ZWT). The experimental Raman scattering reinvestigation of MSE as a function of temperature shows that mode softening does not play an important role in the thermal reaction of MSE. A series of structural phase transitions in the [90 K - 300 K] temperature range is shown for the first time in the MSE crystal by calorimetry and Raman scattering.

Keywords: solid-state reaction; soft mode; calorimetry; Raman scattering

INTRODUCTION

Molecular chemical reactions which proceed thermally in solution can be expected to occur also in the crystalline state. A reaction in a crystal must be accompanied by some structural change in this solid phase[1,2,3]. The simultaneous presence of such a change and a chemical reaction in some molecular solids makes the situation much more complex than in other crystalline solids. In molecular crystals indeed, structural phase transitions are commonly observed phenomena and they are well described by Landau theory. The reaction rate may be much slower in the crystal, but sometimes much faster than in solution. In this former case the concept of phonon assisted reactions has been proposed[4]. In ref. 4 the authors have further postulated that mode softening may play an important role in thermal reactions. So in a reactive system, large amplitude displacements, owing to mode softening, should be expected to assist a solid state reaction[5]. This conclusion is based on an experimental Raman scattering study of a methyl p-dimethylaminobenzenesulfonate crystal (MSE) as a function of temperature in the [120 K - 160 K] range where the compound is not reactive. In the crystalline state indeed, MSE rearranges, at a considerably faster rate than in the melt or in solution, by a thermally enhanced intermolecular chemical reaction, to a zwitterionic product p-trimethylammoniumbenzene-sulfonate ; the reaction occurs at room temperature, and above[6,7,8].

The existence of mode softening as a function of temperature in such a reactive molecular crystal is however not a necessary condition for starting an enhanced thermally solid-state reaction, according to recent theories[2,9]. That's why we decided to make a careful experimental reinvestigation of physical properties of MSE crystals as a function of temperature. In this work experimental methods are described in the following section. The calorimetric results obtained with MSE crystals and our Raman scattering study are presented in the two next sections. The last section is devoted to discussion and conclusion.

Experimental Methods

MSE was synthesized according to ref. 8, using for the first run sulfanilic acid rather than monohydrate. The second and the third runs are the same. The crude product was recrystallized from methanol solution and stored at -70°C. The monocrystalline samples were grown after filtration by slow evaporation of an acetone solution at a temperature near 0°C. Single crystals are obtained as thin plates with approximatively rectangular sides (up to 5 x 7 mm in size) containing (bc) crystallographic plane.

Calorimetric experiments were performed on a Perkin-Elmer DSC7 differential scanning calorimeter connected to a DEC 425 calculator. Temperatures and energy were calibrated using cyclohexane as standard in the [150 K - 230 K] temperature range used for our study. MSE monocrystals weighing about 10 mg were carefully encapsulated in aluminium pans for c_p measurements at a heating rate of 10 K/min. For the first order phase transition, the transition temperature (T_1) was calculated from the intersection of the peak onset and of the base line. For the second order transition, the transition temperature (T_2) corresponds to the half value of the specific heat jump.

For Raman scattering experiment, spectra were recorded with a Dilor-Z 24 spectrophotometer using a krypton laser ($\lambda = 6471$ Å). The resolution of about 1,5 cm^{-1} permitted the observation of Raman lines down to 6 cm^{-1} from the Rayleigh line. The detector was a photomultiplier cooled at about 250 K by a Peltier effect refrigerator. The samples were cooled using a N_2 cryostat in the [90 K - 300 K] temperature range.

Calorimetric Results

Figure 1 shows the specific heat of MSE as a function of temperature in the range [150 K, 230 K] for a monocrystal (10 mg) grown from acetone solution.

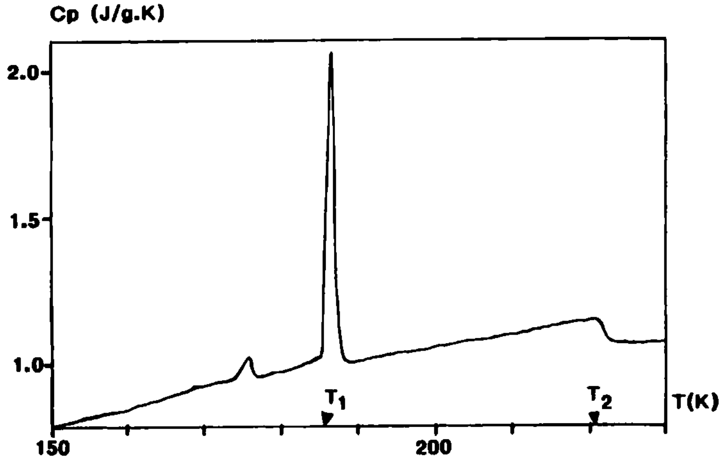

FIGURE 1 Evolution of specific heat of a MSE single crystal as a function of temperature in the [150-230K] temperature range. A first endotherm is observed at T_1 = 185,5 K (first order phase transition) and a second endotherm is observed at T_2 = 221 K (second order phase transition).

A first endotherm at T_1 = 185,5 K has very rapid increase and decrease : this sharp peak can be compared to the ones observed for typical first-order phase transitions as at the melting point of cyclohexane for example. The second endotherm has smoother increase which spreads over 25 K. The transition temperature calculated by considering the endotherm as characteristic of second-order transition is T_2 = 221 K. The third small peak at $T_3 \cong 175$ K corresponds to the melting point of the solvent (acetone) which has been included with very small variable amount in the crystal during the crystallization. The same behaviour is observed in MSE crystals grown from methanol solution but they are too small for permitting to encapsulate a single monocrystal for the calorimetric study.

Raman Scattering Results

The Raman spectra of MSE in the frequency range lying from 5 to 150 cm^{-1} were recorded in the [100K-250K] temperature range. The energy resolution (5 cm^{-1}) is much better than the one of the previous study[4] and is necessary for exploring the possibility of a mode softening. The results of the fitting procedure are summarized on figure 2 in the [0 - 32 cm^{-1}] frequency range. It appears that the first-order phase transition T_1 corresponds to the growing of the new Raman lines. A soft mode which incompletely softens (20 cm^{-1} at T=110 K, 13 cm^{-1} at T_1) may be associated to this transition or to the second order transition at T_2. Actually it is not possible to choose between the two possibilities because the softening mode progressively disappears into the big and broadening mode active in phases I and II (fig. 2) : the soft mode would be not visible in the T_1 - T_2 range even if it was present.

There is only one mode active in phases I and II in the [12 - 32 cm^{-1}] frequency range. This mode has a strong temperature dependence in phases II and III whereas its frequency varies very slightly in phase I, which is monoclinic ($P2_1/c$, Z = 4)[8]. This mode Q belongs to A_g group symmetry in the high temperature phase ; the first coupling term in the Landau expansion as a function of the normal coordinate Q and of the order parameter η is $\eta^2 Q$. The frequency ν is then dependent on η_{eq} in agreement with the equality : $\nu^2 = A + B\,\eta_{eq}^2$. Our study shows that this mode is not a soft mode which would assist a thermally enhanced solid state reaction as pointed out in the previous study[4]. The wrong conclusion of ref. 4 is probably due to the fact that the frequency of this mode in phase I (20 cm^{-1}) corresponds to the low frequency limit from the Rayleigh line on the spectra shown by the authors.

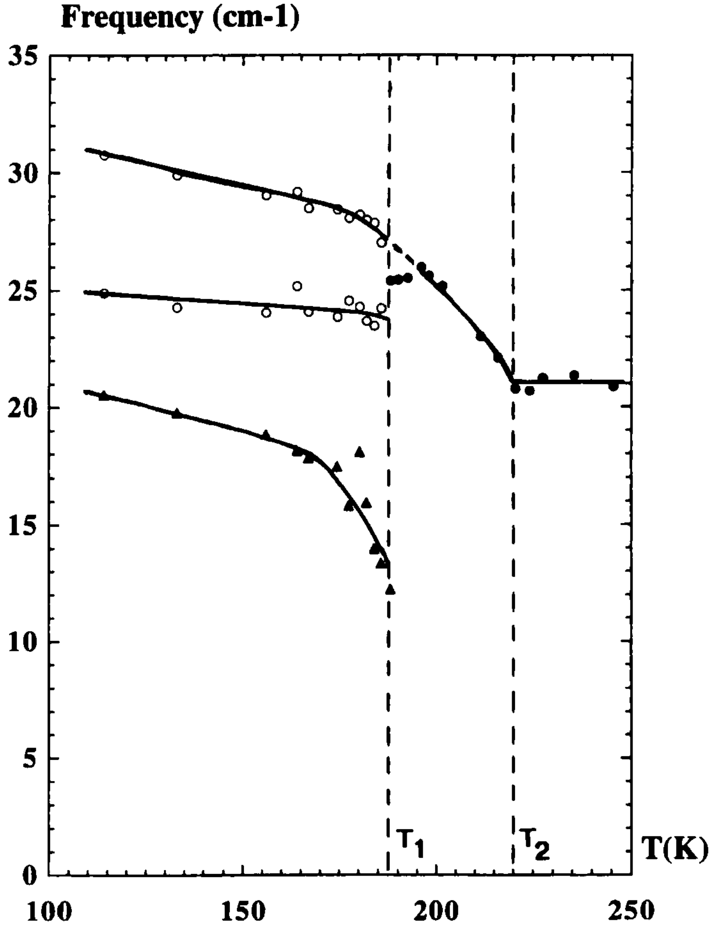

FIGURE 2 Temperature evolution of the frequencies of MSE crystal modes observed by Raman scattering in the [0 - 35 cm^{-1}] frequency range. The drawn line is a guide to the eye for the mode coupled to second-order transition at T_2 = 221 K.

Discussion and Conclusion

Our experimental study of MSE as a function of temperature indicates that the presence of a soft mode is not a prerequisite for assisting a thermally enhanced solid-state reaction[10]. The soft mode observed in ref. 4 is simply a coupled mode involved in the series of the two structural phase transitions which we have detected in MSE crystals. This mode may assist the solid state reaction but with an anharmonic behaviour which does not exceed the one of the other modes. There does not exist at present any experimental proof of the existence of phonon assisted solid-state reactions.

A recent diffraction study[11] shows, in apparent contradiction with our results, that the structure of the MSE crystal is the same at T = 193 K (phase II) and T = 255 K (phase I). One can nevertheless postulate that phase II may be associated to a weak superlattice reflection if it is commensurate or to weak satellites if it is incommensurate.

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