

## SHORT COMMUNICATIONS

LIGHT SCATTERING INVESTIGATIONS OF  $\text{Cs}_2\text{ZnCl}_4$  AT HIGH TEMPERATURES

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$\text{Cs}_2\text{ZnCl}_4$  belongs to the family of crystals typified by  $\text{K}_2\text{SeO}_4$ <sup>1</sup> and  $(\text{NH}_4)_2\text{ZnCl}_4$ <sup>2</sup> which exhibit successive phase transitions and incommensurate phases<sup>3</sup>. Raman and Infrared studies<sup>4,5</sup> of  $\text{Cs}_2\text{ZnCl}_4$  at low temperatures have not revealed any phase transitions. Other members of the family, like  $(\text{NH}_4)_2\text{ZnBr}_4$ <sup>6,7</sup> exhibit incommensurate phases at high temperatures. This paper presents Raman Spectroscopic and light scattering intensity measurements on  $\text{Cs}_2\text{ZnCl}_4$  at high temperatures, as evidence of a possible new phase transition.

Single crystals of  $\text{Cs}_2\text{ZnCl}_4$  were grown at room temperature by slow evaporation of the aqueous solution of cesium chloride and zinc chloride in stoichiometric proportions. Unpolarised Raman Spectra in the spectral region 20–370  $\text{cm}^{-1}$  at room temperature and at 86°K were identical with those reported by Wong<sup>4</sup>. The spectra were obtained by illuminating the crystal with the 4880 Å line from a Spectra Physics Model 164 Argon ion laser with 100 mW power, collecting light scattered at 90° into a SPEX Ramalog double monochromator, and using a RCA C31034 photomultiplier tube and a photon counting system for detection. The crystal was kept at low temperatures in a continuous flow cryostat<sup>8</sup>.

The high temperature spectra were taken with the same spectrometer but with the crystal kept in a high temperature enclosure<sup>8</sup> heated with a variac. The temperature region covered was from 300°–530° ± 2°K and the spectral region 20–370  $\text{cm}^{-1}$  covered the internal vibrational modes<sup>4</sup> of the  $\text{ZnCl}_4^{2-}$  ion and some of the low frequency lattice modes.

Figure 1 shows the integrated intensities of two Raman bands, from 90  $\text{cm}^{-1}$  to 160  $\text{cm}^{-1}$  and from 240  $\text{cm}^{-1}$  to 330  $\text{cm}^{-1}$ , as well as the peak heights of

the three most intense lines at 116  $\text{cm}^{-1}$ , 288  $\text{cm}^{-1}$  and 299  $\text{cm}^{-1}$  at different temperatures. Superimposed on a general smooth decrease of integrated intensities and peak heights as the temperature increases, there is an anomalous peak in all the graphs at about 375 K. It is proposed that the peak is due to a hitherto unreported phase transition, the nature of which has to be understood by further experimentation.

To confirm the existence of the phase transition, the total intensity of light scattered at 90° was measured as a function of temperature. The same high temperature cell was used to heat the crystal. The scattered light from a clear defect free portion of the crystal was directly collected on to the photomultiplier tube. The incident laser beam from a He-Ne laser with 25 mW of power was chopped and the output of the PMT was measured with a lock-in amplifier. Figure 2 shows the graph of the intensity of scattered light versus temperature. Superimposed on a general smooth decrease with increasing temperature, there is a small peak around 340 K which decreases sharply after 380 K. This supports the proposal of a phase transition based on the Raman spectroscopic results. The large fluctuations in dielectric constant near a phase transitions are responsible for the anomalous increase in light scattering.

The absence of structural data on this crystal at high

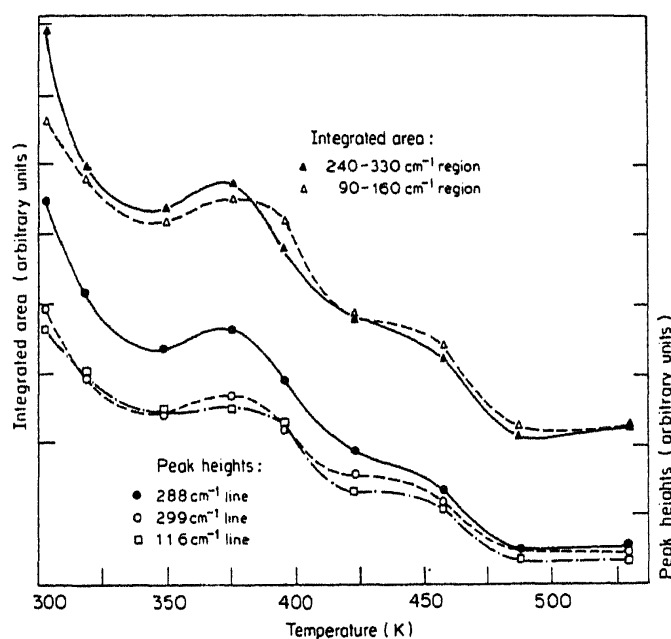
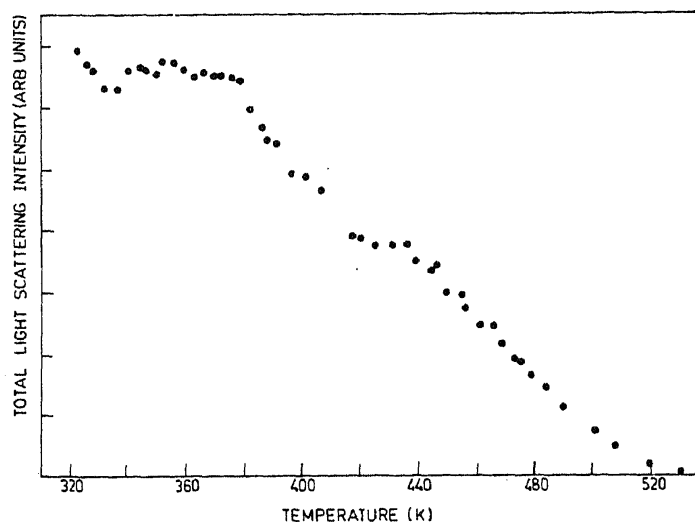


Figure 1. Integrated areas and peak heights vs temperature.

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**Figure 2.** Total intensity of light scattering vs temperature.

temperatures prevents more detailed correlation of the light scattering results with the nature of the structural changes at the phase transition.

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## MONOTHIO- $\beta$ -DIKETONE DERIVATIVES OF INDIUM, GERMANIUM AND TIN

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MONOTHIO- $\beta$ -diketones as ligands are quite different from  $\beta$ -diketones. The consequence of gradual replace-

ment of oxygen by sulphur can be illustrated by examining the complexes of the thio-analogue. In contrast to the later transition metals, the chemistry of main group and early transition elements with monothio- $\beta$ -diketone is very little known<sup>1-3</sup>. The present communication reports our attempts to prepare and characterise some indium(III), germanium(IV), tin(II) and tin(IV) complexes of a few monothio- $\beta$ -diketones<sup>4-6</sup>.

Reactions were carried out under anhydrous conditions in dry nitrogen atmosphere. Solvents were dried by standard methods. Monothio- $\beta$ -diketones R'CSCH<sub>2</sub>COR'' (R' = Ph, Me; R'' = Ph, Me, C<sub>6</sub>H<sub>4</sub>Me-P, C<sub>6</sub>H<sub>4</sub>Br-P) were synthesised using usual procedures<sup>2-4, 7</sup> by Claisen condensation. InCl<sub>3</sub> and GeCl<sub>4</sub> were purchased from Fluka. SnCl<sub>4</sub> was also prepared by the normal procedure<sup>8</sup>. Anhydrous SnCl<sub>2</sub> was obtained from SnCl<sub>2</sub>·2H<sub>2</sub>O by the standard method<sup>9</sup>.

The m.p. of the compounds was determined in sealed capillary tube. Elemental analyses (Ge, In<sup>10</sup>, Sn and S) were carried out gravimetrically<sup>11</sup>. IR spectra were recorded as Nujol mulls using KBr pellets and polythene sheet in the range 4000–200 cm<sup>-1</sup> on Perkins Elemer 621 spectrometer. PMR spectra were recorded on EM-360 60 MHz in CDCl<sub>3</sub> with TMS as an internal standard. Molecular weights were determined cryoscopically in benzene.

### (a) Preparation of dichloro bis(monothio- $\beta$ -diketonato) Ge(IV) complexes

GeCl<sub>4</sub> and the monothio- $\beta$ -diketone were mixed in dry hexane (~50 ml) in 1:2 molar ratio and the mixture refluxed for 30 hr under nitrogen atmosphere and cooled. The contents were filtered and the solid was washed with dry hexane. The details are tabulated in table 1.

### (b) Preparation of bis(monothio- $\beta$ -diketonato) Sn(II) and Sn(IV) complexes

In a solution of SnCl<sub>2</sub> in absolute methanol stoichiometric amounts of ligand and potassium acetate (sodium acetate in case of SnCl<sub>4</sub>) in abs. methanol were added dropwise while stirring. Stirring was continued for 3 hr at room temperature (25°C). Solid products separated out, were filtered and washed with abs. methanol and recrystallized from chloroform/methanol (1:3) mixture. Details are given in table 1.

### (c) Preparation of bis- and tris(monothio- $\beta$ -diketonato) indium(III) complexes

In a solution of anhydrous InCl<sub>3</sub> in abs. methanol, stoichiometric amounts of the ligand and sodium