LIGHT SCATTERING INVESTIGATIONS OF 
Cs₂ZnCl₄ AT HIGH TEMPERATURES

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Cs₂ZnCl₄ belongs to the family of crystals typified by 
K₂SeO₄¹ and (NH₄)₂ZnCl₄² which exhibit successive 
phase transitions and incommensurate phases³. 
Raman and Infrared studies⁴-⁵ of Cs₂ZnCl₄ at low 
temperatures have not revealed any phase transitions. 
Other members of the family, like (NH₄)₂ZnBr₄⁶-⁷ 
exhibit incommensurate phases at high temperatures. 
This paper presents Raman Spectroscopic and light 
scattering intensity measurements on Cs₂ZnCl₄ at 
high temperatures, as evidence of a possible new phase 
transition.

Single crystals of Cs₂ZnCl₄ 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 cm⁻¹ at room 
temperature and at 86 K were identical with those 
reported by Wong⁴. The spectra were obtained by 
iluminating the crystal with the 4880 A 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 cryostat⁸.

The high temperature spectra were taken with the 
same spectrometer but with the crystal kept in a high 
temperature enclosure⁹ heated with a variac. The 
temperature region covered was from 300⁰-530⁰ 
± 2 K and the spectral region 20-370 cm⁻¹ covered 
the internal vibrational modes⁴ of the ZnCl₄²⁻ ion 
and some of the low frequency lattice modes.

Figure 1 shows the integrated intensities of two 
Raman bands, from 90 cm⁻¹ to 160 cm⁻¹ and from 
240 cm⁻¹ to 330 cm⁻¹, as well as the peak heights of 
the three most intense lines at 116 cm⁻¹, 288 cm⁻¹ and 
299 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 tempera-
ture. Superimposed on a general smooth decrease with 
increasing temperature, there is a small peak around 
340 K which decreases sharply after 380 K. This sup-
ports 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

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Figure 1. Integrated areas and peak heights at various 
temperatures.
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-β-DIKETONE DERIVATIVES OF INDIUM, GERMANIUM AND TIN

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Monothio-β-diketones as ligands are quite different from β-diketones. The consequence of gradual replacement 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-β-diketone is very little known. 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-β-diketones.

Reactions were carried out under anhydrous conditions in dry nitrogen atmosphere. Solvents were dried by standard methods. Monothio-β-diketones R'CSCH₂COR" (R' = Ph, Me; R" = Ph, Me, C₆H₄Me-P, C₆H₄Br-P) were synthesised using usual procedures by Claisen condensation. InCl₃ and GeCl₄ were purchased from Fluka. SnCl₄ was also prepared by the normal procedure. Anhydrous SnCl₂ was obtained from SnCl₂·2H₂O by the standard method.

The m.p. of the compounds was determined in sealed capillary tube. Elemental analyses (Ge, In₁₀, Sn and S) were carried out gravimetrically. IR spectra were recorded as Nujol mulls using KBr pellets and polythene sheet in the range 4000–200 cm⁻¹ on Perkins Elemer 621 spectrometer. P.M.R spectra were recorded on EM-360 60 MHz in CDCl₃ with TMS as an internal standard. Molecular weights were determined cryoscopically in benzene.

(a) Preparation of dichloro bis(monothio-β-diketono) Ge(IV) complexes

GeCl₄ and the monothio-β-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-β-diketonato) Sn(II) and Sn(IV) complexes

In a solution of SnCl₂ in absolute methanol stoichiometric amounts of ligand and potassium acetate (sodium acetate in case of SnCl₄) 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-β-diketono) indium(III) complexes

In a solution of anhydrous InCl₃ in abs. methanol, stoichiometric amounts of the ligand and sodium