undergoes a ferroelastic phase transition at 202° K from the room temperature orthorhombic Pccm phase to a low temperature P2/11n phase. Alexandrov et al. and Delfino et al. have studied the thermal and dielectric properties of LiCsSO₄ (LCS) and it has been suggested that it undergoes a continuous phase transition. While reporting the structural and physica properties of LCS Alexandrov et al. mentioned that the pressure dependence of dielectric constant as a function of temperature shows a negative shift of $T_c$ with $dT_c/dP = -2.6^\circ K/Kbar$. However, this value differs much from the theoretically expected value of $dT_c/dP$ based on Ehrenfest relatin. Further, details of their pressure study have not been given. In view of this, a detailed study of the effect of hydrostatic pressure on the dielectric properties of LCS was taken up and the results obtained therein are reported here.

For the purpose of measuring the dielectric constant at high pressures a piston-cylinder type pressure cell was used. The capacitance of the sample was measured using a Marconi Universal Bridge TF 1313A operating at 1 kHz. The measurement was carried out along the $b$-axis of the crystal. A bath-type cryostat was used to cool the pressure cell. The details of the instrumentation, calibration and the measurement were published earlier. The observed dielectric anomalies along the $b$-axis of LCS crystal in the heating run under various hydrostatic pressures are shown in figure 1. It is seen from these plots that the phase transition tempera-

---

**PRESSURE EFFECT ON THE DIELECTRIC PROPERTIES OF LiCsSO₄**

**B. RAGHUNATHA CHARY,**
**M. N. SHASHIKALA and H. L. BHAT**

*Department of Physics, Indian Institute of Science, Bangalore 560 012, India.*

LiCsSO₄ belongs to the family of crystals with the general formula M' M'' BX₄ (M': Li, Na etc; M'': K, Rb, Cs, NH₄ etc; BX₄: SO₄, SeO₄, BeF₄). It

---

**Figure 1.** Plots of $\varepsilon_r$ vs $T$ under various hydrostatic pressures.
ture \( T_c \) shifts towards the lower side with the increase of pressure and the peak value of dielectric constant decreases. The shape of the dielectric curve does not show any remarkable change with pressure indicating that the transition continues to be of second order even up to 7.4 Kbars. The plots of \( \frac{1}{(\varepsilon_b - \varepsilon_w)} \) vs temperature under selected pressures are shown in figure 2. The quantity \( \varepsilon_w \) is taken as equal to \( n_i^2 \), where \( n_i \) (= 1.519) is the refractive index of the crystal. It can be seen that at a pressure of 0.5 Kbar, the Curie-Weiss law is obeyed only over a narrow temperature range of 197° K–201.5° K below the phase transition and in a wider range of 201.5° K–217° K above phase transition. These ranges widen appreciably at higher pressures.

The variation of \( T_c \) with pressure is shown in figure 3. It is seen that with increase of pressure, the transition temperature \( T_c \) decreases. As can be noticed, the change in \( T_c \) with pressure is linear up to 5 Kbars above which it deviates from linearity. By measuring the slope of the linear portion of this plot (below 5 Kbars), the rate of change of \( T_c \) with pressure \( P \), that is \( \frac{dT_c}{dP} \) is evaluated to be \(-1.25\)° K/Kbar, as against a value of \(-2.6\)° K/Kbar obtained by Aleksandrov et al.\(^5\). It may be noted that the value of \( \frac{dT_c}{dP} \) obtained in the present work is closer to the value of \(-1.0 \pm 0.5\) K/Kbar obtained, making use of the Ehrenfest relation\(^5\). The negative \( \frac{dT_c}{dP} \) is presumably a consequence of the volume thermal expansion coefficient of LCS showing a negative anomaly at the transition. It is to be noted here that in contrast to LCS, a number of other double sulphates such as LiNH₄SO₄, RbHSO₄ and NH₄HSO₄ show a positive \( \frac{dT_c}{dP} \). Based on the Ehrenfest relation, one would expect that the volume thermal expansion coefficients of these crystals show positive anomalies across the phase transition. Table 1 gives the experimental and calculated values of \( \frac{dT_c}{dP} \), thermal expansion and specific heat data for the above crystals. The data for LiCsSO₄ are also given for comparison. It can be seen that in crystals showing positive \( \frac{dT_c}{dP} \), positive anomalies in \( \beta \) were observed at \( T_c \)\(^{10,11}\).

Samara et al.\(^{15,16}\) based on the data of a number of crystals exhibiting phase transitions have observed that \( T_c \) decreases with pressure for the transitions associated with zone-centre soft modes and increases for those associated with zone-boundary soft modes. But our studies on Raman spectra of LCS in the lattice region across the phase transition did not reveal the presence of any optical soft mode\(^4\). It is therefore concluded that LCS is elastically soft and optically hard ferroelastic\(^7\).

We thank Prof. P. S. Narayanan for his advice and help in this work.

9 July 1986
### Table 1 Thermodynamic properties of NH$_4$HSO$_4$, RbHSO$_4$, LiNH$_2$SO$_4$ and LiCsSO$_4$ crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$T_c$(°K)</th>
<th>$\Delta \beta$ *10$^{-6}$K$^{-1}$</th>
<th>$\Delta C_p$ J mol$^{-1}$°K</th>
<th>$dT_c/dP$ (°K/Kbar)</th>
<th>Experimental</th>
<th>Ehrenfest relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$HSO$_4$</td>
<td>270.9</td>
<td>80.5</td>
<td>12.2$^{12}$</td>
<td>14$^{13}$</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>RbHSO$_4$</td>
<td>264.5</td>
<td>63</td>
<td>9.5$^{12}$</td>
<td>12$^a$</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>LiNH$_2$SO$_4$</td>
<td>459.6</td>
<td>600$^7$</td>
<td>197.5$^{14}$</td>
<td>9.8$^7$</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>LiCsSO$_4$</td>
<td>202.07</td>
<td>-30$^7$</td>
<td>43$^7$</td>
<td>-1.25</td>
<td>-1.0</td>
<td></td>
</tr>
</tbody>
</table>

Note: Numbers in superscript denote references.

* $\Delta \beta$ : Change in volume thermal expansion coefficient across the transition.

* $\Delta C_p$ : Change in specific heat across the transition.


---

**SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM(II) WITH 1-(2-THIAZOLYLazo)-2-NAPHTHOL IN PRESENCE OF TRITON X-100**

M. C. ESHWAR and G. V. RATHAIAH
Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India.

Even though pyridylazo and thiazolylazo dyes find wide application in analytical reagents, no thiazolylazo derivative has been employed for the determination of beryllium(II). It has been found that the reaction between 1-(2-thiazolylazo)-2-naphthol, TAN, and beryllium(II) is suitable for spectrophotometric determination of beryllium.

Absorbance measurements were made on Spectromom 204 UV-visible spectrophotometer and absorption spectra recorded on Superscan 3 UV-visible spectrophotometer. A Cambridge pH meter was employed for pH measurements. Stock solution of beryllium(II), prepared from beryllium nitrate tetrahydrate (E Merck), was standardized gravimetrically. A 0.1% (w/v) methanolic solution