Figure 1. A reproduction of the original tracing of the occultation event as recorded on the DC chart recorder.

is elongated and the lower limit on its size along the direction of the track is 119 ± 5 km. Finally, the difference in the observed and predicted times can be used to improve the orbital elements of the asteroid.

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PRESSURE EFFECT ON THE DIELECTRIC PROPERTIES OF LiCsSO₄

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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

undergoes a ferroelastic phase transition at 202° K from the room temperature orthorhombic Pcmn phase to a low temperature P2₁/n phase[1]. Aleksandrov et al[2] and Delfino et al[3] 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 physical properties of LCS Aleksandrov et al[2] mentioned that the pressure dependence of dielectric constant as a function of temperature shows a negative shift of T_c with $dT_c/dP = -2.6°$ K/Kbar. However, this value differs much from the theoretically expected value of dT_c/dP based on Ehernfest relation. 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[4,5].

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-
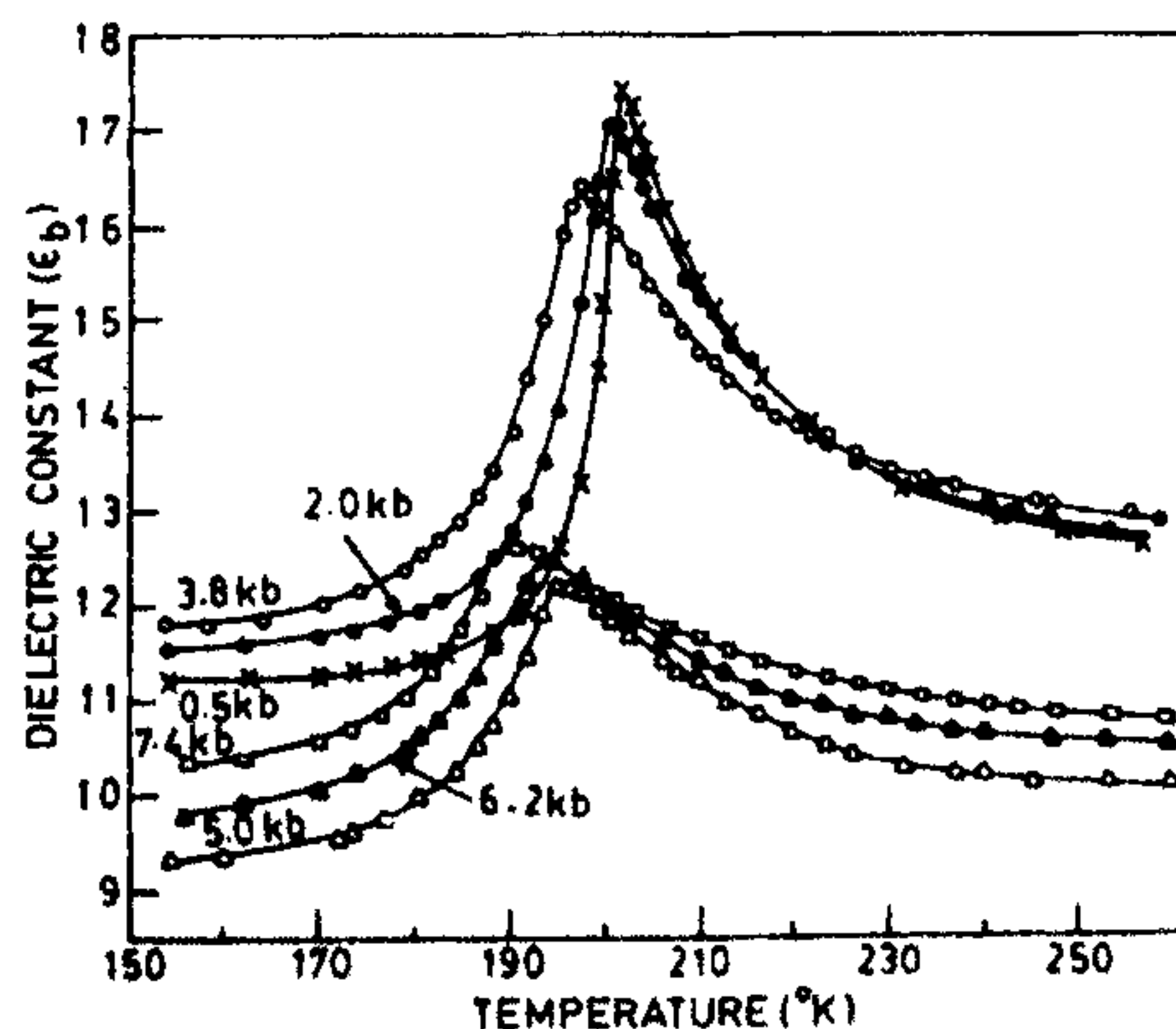

Figure 1. Plots of ϵ_b vs T under various hydrostatic pressures.

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 $1/(\epsilon_b - \epsilon_\infty)$ vs temperature under selected pressures are shown in figure 2. The quantity ϵ_∞ is taken as equal to n_b^2 where n_b $(= 1.519)$ is the refractive index of the crystal[6]. 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 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[2]. It may be noted that the value of dT_c/dP obtained in the present work is closer to the value of -1.0 ± 0.5 K/Kbar obtained, making use of the Ehrenfest relation[2]. The negative 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
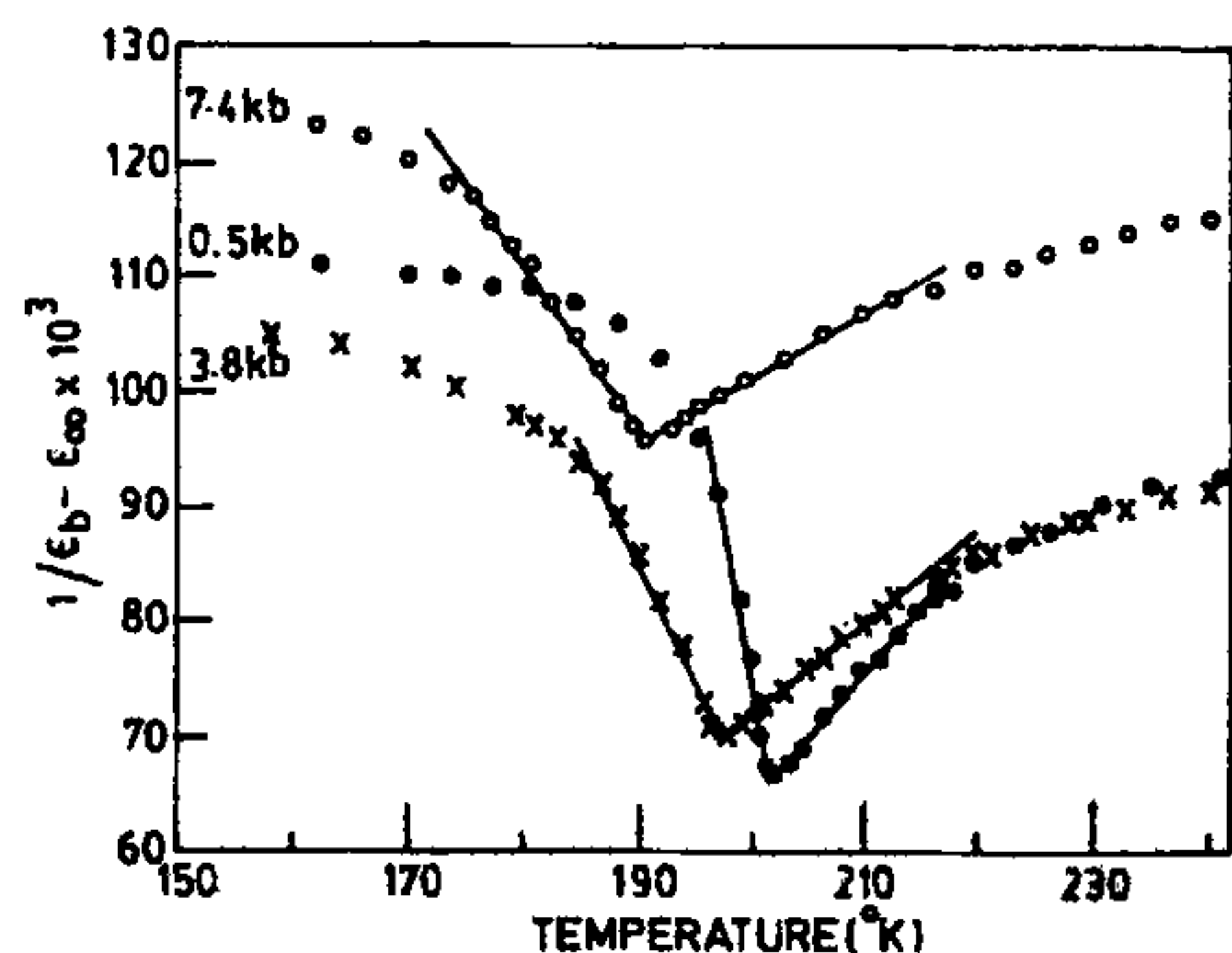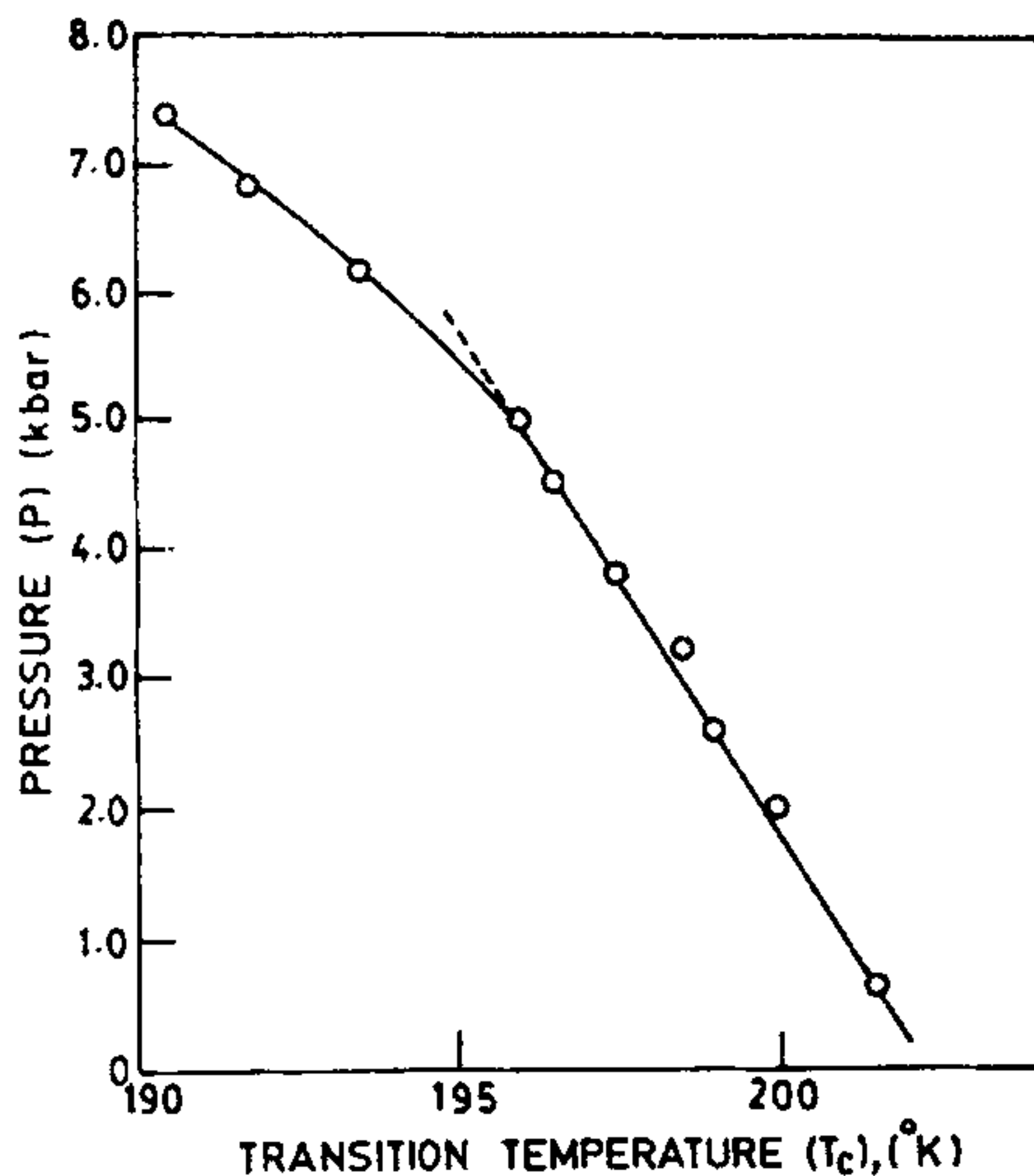

Figure 3. Variation of T_c with pressure.

double sulphates such as $LiNH_4SO_4$, $RbHSO_4$ and NH_4HSO_4 show a positive dT_c/dP[7–9]. 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 dT_c/dP, thermal expansion and specific heat data for the above crystals. The data for $LiCsSO_4$ are also given for comparison. It can be seen that in crystals showing positive dT_c/dP, positive anomalies in β 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[17].

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

Figure 2. Plot of $1/(\epsilon_b - \epsilon_\infty)$ vs T at three different pressures.

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Table 1 *Thermodynamic properties of NH_4HSO_4, $RbHSO_4$, $LiNH_4SO_4$ and $LiCsSO_4$ crystals*

Crystal	T_c(°K)	$\Delta\beta^*$ $10^{-6}\cdot K^{-1}$	ΔC_p J. $mol^{-1}\cdot$°K	dT_c/dP (°K/Kbar) Experiment	Ehrenfest relation
NH_4HSO_4	270.9	80.5	12.2[12]	14[13]	11.3
$RbHSO_4$	264.5	63	9.5[12]	12[8]	11.1
$LiNH_4SO_4$	459.6	600[7]	197.5[14]	9.8[7]	8.8
$LiCsSO_4$	202.07	−30[2]	43[2]	−1.25	−1.0

Note : Numbers in superscript denote references.
*$\Delta\beta$: Change in volume thermal expansion coefficient across the transition.
*ΔC_p : Change in specific heat across the transition.

1. Kruglik, A. I., Simonov, M. A., Zhelezin, E. P. and Belov, N. V., *Sov. Phys. Dokl.*, 1979, **24**, 596.
2. Aleksandrov, K. S., Zherebtsova, L. I., Iskornev, I. M., Kruglik, A. I., Rozanov, O. V. and Flerov, I. N., *Sov. Phys. Solid State*, 1980, **22**, 2150.
3. Delfino, M., Loiacano, G. M., Smith, W. A., Shaulov, A., Tsuo, Y. H. and Bell, M. I., *J. Solid State Chem.*, 1980, **31**, 131.
4. Raghunatha Chary, B., *Ph. D. Thesis, Indian Institute of Science, Bangalore*, 1985.
5. Raghunatha Chary, B., Bhat, H. L. and Narayanan, P. S., *Proc. 3rd Natl. seminar on ferroelectrics and dielectrics*.
6. Anistratov, A. T., Zamkov, A. V., Kot, L. A., Stdovitskaya, I. N. and Shabanova, L. A., *Ferroelectrics*, 1983, **48**, 103.
7. Shimizu, H., Oguri, A., Yasuda, N. and Fujimoto, S., *J. Phys. Soc. Jpn.*, 1978, **45**, 565.
8. Gesi, K. and Ozawa, K., *J. Phys. Soc. Jpn.*, 1975, **38**, 459.
9. Tamaki, A. and Fujimura, T., *J. Phys. Soc. Jpn.*, 1983, **52**, 2922.
10. Iskornev, I. M. and Flerov, I. N. *Sov. Phys. Solid State*, 1977, **19**, 605.
11. Iskornev, I. M. and Flerov, I. N. *Sov. Phys. Solid State*, 1978, **20**, 1531.
12. Aleksandrov, K. S., Anistratov, A. T., Blat, D. Kh., Zherebtsova, L. I., Zinenko, V. I., Iskornev, I. M., Melnikova, S. V. and Flerov, I. N., *Ferroelectrics*, 1976, **12**, 191.
13. Polandov, I. N., Mylov, V. P. and Strukov, B. A., *Sov. Phys. Solid State*, 1969, **10**, 1754.
14. Loicono, G. M., Delfino, M., Smith, W. A., Bell, M. I., Shaulov, A. and Tsuo, Y. H.,
Ferroelectrics, 1980, **23**, 89.
15. Samara, G.A., Sakudo, T. and Yoshimitsu, K., *Phys. Rev. Lett.*, 1975, **35**, 1967.
16. Samara, G. A., *Comm. Solid State Phys.*, 1977, **8**, 13.
17. Wadhawan, V. K., *Phase transitions*, 1982, **3**, 50.

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

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EVEN though pyridylazo and thiazolylazo dyes find wide application[1,2] as 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-naph-thol, 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[3]. A 0.1% (w/v) methanolic solution