INTRODUCTION

In the field of solids, the properties of the alkali halides have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a progressively better understanding of some of the most interesting properties. Knowledge of the behaviour of thermal expansion is a necessary adjunct for the calculation of many mechanical and thermodynamical properties of alkali halides. But when the literature about the variation of lattice constants with temperature by X-ray methods is examined, we find that there are hardly any attempts to study the crystals as a group. Scattered data are available on lattice constant variation (and hence on thermal expansion variation) with temperature, in some cases up to the melting point and in others within a limited range of temperature. In many cases where data up to melting point are available, there are wide discrepancies. For example, the thermal expansion of sodium chloride at 700°C determined by
Lunken and Dannöhl (1934) is $73.8 \times 10^{-6} (\text{C}^{-1})$, while the corresponding value of Leaatetter and Hewsham (1969) is $63.9 \times 10^{-6} (\text{C}^{-1})$. Similarly, the X-ray value of the thermal expansion of CsI at 25°C given by Johnson, Agron and Bredig (1955) is about 20 per cent lower than the precision X-ray determination of Ryser and Hambling (1951). Similar large discrepancies are noticed in the case of several alkali halides. Moreover, most of the X-ray work on thermal expansion is done by photographic method with its inherent weaknesses.

Lawson (1950) pointed out that for a perfect crystal the coefficient of thermal expansion $\alpha$ should not vary with temperature and that the increase of $\alpha$ with temperature, as is observed in the case of alkali halides, is due to the role of lattice defects. Mott (1940) has shown that the concentration of Frenkel defects in alkali halides is very small and hence Schottky defects predominate. If it is really so, the X-ray and macroscopic thermal expansion must differ. Fischmeister (1956) has shown that the variation of $\alpha$ with temperature can be explained by the Debye-Grüneisen theory and has drawn graphs in support of his explanation. His work was criticised by Fletcher (1957) and Eastabrook (1957) who showed that the agreement between the Debye-Grüneisen theory and
experiment is not very satisfactory.

Merriam et al (1962) have shown that for NaCl above 500°C the temperature dependence of $\alpha$ can be related to the thermally generated Schottky defects. The thermal expansion is considered to consist of two parts - a "normal" contribution and an "anomalous" part. They studied the data of Eucken and Dannöhl (1934) on thermal expansion of NaCl and showed that the anomalous part increases exponentially with temperature with an activation energy of vacancy pair formation consistent with that deduced from ionic conductivity studies.

It has been deduced theoretically by Catz (1955) that in the case of thermal expansion a 'law of corresponding states' should hold and he has shown that the graph between the reduced expansion $\alpha/\alpha_m$ and the reduced temperature $T/T_m$ for cubic metals is a straight line in the range $0.2 < T/T_m < 0.7$ ($T_m$ is the melting point and $\alpha_m/2$ is the coefficient of thermal expansion at $T=1/2T_m$).

A study limited to any one alkali halide, as has been done by most authors, naturally cannot throw any substantial light on the general characteristic behaviour of the entire group of alkali halides. For this
purpose, it is necessary to study several alkali halides under identical conditions of experimentation and measurement. Such a compilation of results should by itself prove to be of great value to investigators in this field of study, specially because such a group study has not been attempted before.

The present investigation was, therefore, undertaken

(i) to provide accurate X-ray data on the thermal expansion of alkali halides by employing a diffractometer, Geiger Counter, ratemeter, an automatic chart recorder and a specially designed high temperature attachment;

(ii) to study the role of lattice defects on the thermal expansion of alkali halides;

(iii) to examine whether the law of corresponding states holds for alkali halides.

The alkali halides examined are sodium chloride, sodium fluoride, potassium chloride, caesium chloride (CsCl phase), caesium bromide, rubidium chloride and lithium fluoride.