CHAPTER I

INTRODUCTION

In the field of solids, the properties of metals have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a better and better understanding of some of the most interesting properties. Various theoretical structures called the force-constant models, phenomenological models and fundamental theories have been evolved to understand a metal, especially the ion-electron interaction in it. But no successful model has yet been developed which can explain experimental observations at low as well as high temperatures. High temperature phenomena present special difficulties due to anharmonicity of the lattice vibrations. Under these circumstances, precise experimental determinations (of quantities like thermal expansion, Debye Θ etc.) and possible correlations between various physical quantities assume great importance since such determinations and correlations will be of immense use to theoreticians.
When the literature about the variation of lattice constants and Debye temperatures with temperature by X-ray methods is examined, it is found that there are hardly any attempts to study the metals 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 aluminium at 200°C determined by Simmons and Balluffi (1960a) is 19% lower than the value of Esser, Elender and Bungardt (1938). In the case of silver, the thermal expansion determined by Spreadborough and Christian (1959) is almost independent of temperature up to about 550°C and the value is 15% lower than the value of Simmons and Balluffi (1960b). In the case of (X-ray or neutron) Debye temperatures, the variation in the case of aluminium is from 368±03 K and for silver it is from 191±239 K at room temperature. Similar large discrepancies can be noticed in the case of several metals. Moreover, most of the X-ray work on 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 and metals, is due to the role of lattice defects.

Merriam et al (1962) have shown that above about 500°C the temperature dependence of the thermal expansion of sodium chloride 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. The anomalous part is shown to increase 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 Cartz (1955) that in the case of physical properties which depend on atomic vibrations in crystals a "law of corresponding states" should hold. For example, he has shown that the graph between the reduced expansion \( \frac{\alpha}{(\alpha)_{m/2}} \) and the reduced temperature \( \frac{T}{T_m} \) for cubic metals is a straight line in the range \( 0.2 < \frac{T}{T_m} < 0.7 \). (Here \( T_m \) is the melting point and \( (\alpha)_{m/2} \) is the coefficient of thermal expansion at \( T=\frac{1}{2}T_m \).

A study limited to any one metal, as has been done by most authors, naturally cannot throw any substantial light on the general characteristic behaviour of the entire group of metals. For this purpose, it is necessary to study several metals 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 been hardly attempted before. (The present thesis contains the first report of a series of investigations to be undertaken on fcc metals).

The present investigation was, therefore, undertaken

(i) to provide accurate X-ray data on the thermal expansion and Debye temperature of metals by employing a diffractometer, scintillation counter, ratemeter, an automatic chart recorder, a specially designed high temperature attachment and a computer (to deduce suitable equations from observations).

(ii) to study the role of lattice defects in the thermal expansion of metals.

(iii) to examine how far the "law of corresponding states" holds for the metals investigated with special reference to thermal expansion and Debye-Waller factor since these properties depend on atomic vibrations.
(iv) to examine the lattice dynamics of metals and especially the theories of anharmonicity since the rapid increase of thermal expansion near the melting point may be the result of higher order anharmonic terms.

Metals examined in the present investigation are silver and aluminium.