COMPRESSIBILITY OF SOLIDS AND TAIT'S LAW:
I: P–V RELATIONSHIPS OF THE ALKALI METALS

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Abstract—It has been shown, using both Swenson's data at 4·2°K and Bridgman's data at room temperature, that the alkali metals, which do not follow Bridgman's empirical law, do follow Tait's Law. Both Bridgman's empirical equation and Levitt's high pressure empirical approach are shown to be special cases of Tait's Law. Bridgman's series of data up to 40,000 kg/cm^2 is shown to be about as reliable as his 100,000 kg/cm^2 data. Use of the Tait equation, which is founded on the strict theoretical ground of association theory, allows data to be smoothed on a theoretical basis rather than on a strictly empirical one. Since Tait's Law is derived without assumptions from the general association equation of state, it has now been shown that this equation of state is applicable to gases, liquids and most likely solids. Data for solids which is not consistent with this treatment should be held as suspect or non-continuous over the pressure range being considered.

1. INTRODUCTION

A number of investigations[1–4] have shown empirically that Tait's Law [equation (1)] which describes the isothermal compressibility, is obeyed quite exactly by large numbers of pure liquids, organic and inorganic; by mixture of liquids; and by solutions of ionic salts.

$$-\left(\frac{\partial v}{\partial p}\right) = \frac{J}{L+p} \tag{1}$$

This empirical law has been theoretically derived from the association equation of state[5,6] and the meaning of the experimental parameters, J and L, has been given in terms of the quantities entering from association theory.[7] From this development by association theory it appears that the structure of liquids is essentially similar to that of poly-crystalline solids. It is well known that poly-crystalline solids consist of small crystallites in which the arrangement of the atoms or molecules is symmetrical; these crystallites are connected by defect regions which contain smaller aggregates or single atoms. In a similar way, it appears that liquids consist of clusters of atoms or molecules separated by defect regions, which contain voids and smaller aggregates. Just as the crystallites in polycrystalline solids are held together by defect regions, so the liquid clusters are held together by the defect molecules.

The outstanding difference between the two states is concerned with the differences in symmetry of packing that exist. While solid crystallites exhibit exact symmetries which may be 3-, 4-, or 6-fold (or even less), the symmetries in liquids are not exact and are approximately 5-fold. By exact symmetries it is meant that no matter what the order of the symmetry is, each atom or molecule in the crystal array has an assigned position around which it vibrates. The balance of forces in the array is such that the equilibrium position of each atom can be considered fixed or, put in other words, that there is a high potential barrier around each site. On the other hand, in liquids the symmetry in the cluster is apparently an approximate 5-fold symmetry.[8] In contrast to the exact symmetries existing in solids, atoms packed in 5-fold symmetry give rise to many small voids in the structure. Because of the arrangement of these voids, many equivalent structures (degenerate) exist. The energy barrier between these structures appears to be exceedingly small, so that the atoms in the liquid structure upon vibration do not always return to a fixed equilibrium position.