

Liquid-like defects in superionic fluorites

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Abstract. A model based on the presence of two-level systems identified with defect clusters is used to study different properties of superionic lead fluoride and calcium fluoride. The high degeneracy of the higher level indicates a liquid-like arrangement of anions within the cluster.

Keywords. Superionic conductors; fluorites; defect cluster; two-level systems.

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1. Introduction

The fluorite group of superionic conductors like PbF_2 , CaF_2 , BaF_2 , SrCl_2 etc are now being widely studied. It has been shown that a model assuming presence of two-level systems (TLS) in fluorites can account for the anomalous properties observed in strontium chloride Makur and Ghosh (1989a). These properties are—(i) a Schottky peak in the C_v vs T curve at the temperature T_c (Schroter and Nolting 1980), (ii) lowering of the bulk modulus around T_c (Cao Xuan An 1977), (iii) a peak in the thermal expansion (Roberts and White 1986), (iv) rapid rise in the ionic conductivity below T_c (Van Gool 1973) and an anomaly in the dielectric constant (Kosacki and Zalibowsky 1988). The TLS can be identified with defect clusters similar to those observed in the extensive neutron scattering studies by Hutchings *et al* (1984).

In our study it has been observed that the peculiarity of the TLS is their abnormal high density of states corresponding to considerable spatial disorder within a defect cluster. This indicates a localized amorphous arrangement of a group of anions (the current carriers). In this work we analyze the possible implications of this feature and present the calculation of the above mentioned properties for PbF_2 and CaF_2 and look for systematic trends in their behaviour. The results for SrCl_2 and the dielectric constant for PbF_2 have been given in Makur and Ghosh (1989a, b).

2. The TLS model in brief

It is now more or less established that at low temperatures the compounds studied have a perfect fluorite structure and as temperature rises Frenkel defects are formed. One or more Frenkel pairs together with the relaxed neighbours form stable defect clusters.