

## Dielectric properties of superionic lead fluoride

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**Abstract.** Recent experimental studies show that the dielectric constant of lead fluoride increases rapidly as the superionic transition temperature  $T_c$  is approached. In this work the static dielectric constant ( $\epsilon$ ) is calculated theoretically for low and high temperature limits. Assuming conduction to take place through a percolation mechanism,  $\epsilon$  is found to diverge at the threshold temperature  $T_{th}$  where ionic conduction starts.

**Keywords.** Superionic conductor; dielectric constant; percolation, teso-level-system.

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### 1. Introduction

The high ionic conductivity of  $\text{PbF}_2$ , at a relatively low temperature (around 700 K) and the associated specific heat anomaly, have received a lot of attention in recent times (Schröter and Nölting 1980; Carr *et al* 1978). Extensive studies on quasielastic scattering of neutrons by the fluorites have been made by Hutchings *et al* (1984) which indicate the existence of defect clusters. There have been, however, relatively few studies of the dielectric properties (Kosacki and Zalibowsky 1988) which may provide a clue to the processes responsible for the anomalies observed in such materials. The work of Kosacki and Zalibowsky (1988) shows that there is a sharp rise in the dielectric constant ( $\epsilon$ ) of  $\text{PbF}_2$  close to the temperature  $T_c$  where the specific heat anomaly occurs,  $\epsilon$  increases here by a factor of  $10^5$ .

It has been shown (Makur and Ghosh 1989) that the high ionic conductivity of the fluorites may be described by a percolation mechanism. In mixed conductor insulator systems such as carbon-in-wax a divergence of the dielectric constant has been observed near the percolation threshold (Chou and Jaw 1988). However the conduction mechanism in superionic fluorites is different from the systems where percolation is usually studied. In superionic materials the current is carried by ions through a hopping like mechanism whereas in usual conduction electrons are the current carriers. In this work we suggest an approach for estimating the static dielectric constant  $\epsilon(T)$  which is consistent with the abnormal ionic conductivity of  $\text{PbF}_2$ .

### 2. Model for ionic conduction and dielectric constant

Frenkel pairs are formed in the fluorites at finite temperatures and they are responsible for the ionic conduction. The defects are found to be present in clusters (Hutchings

*et al* 1984) which may include one or two Frenkel pairs and relaxed nearest and next nearest neighbours surrounding the interstitial anion. The clusters are in dynamic disorder, continually forming and breaking up again with a lifetime of about  $10^{-12}$ . The defect cluster has a non-zero dipole moment so in the presence of an external electric field, the dipole tries to orient in the field direction. The defect cluster, cannot, of course, rotate as a whole, but when it breaks up and reforms, it tends to lower the energy by aligning its dipole moment with the external field. At relatively low temperatures the dipoles are isolated and interaction between them can be neglected. Under such conditions the net dipole moment  $P$  per unit volume in presence of an external field  $E$  can be written using the well known expression for a dilute gas of dipoles (Dekker 1986) as

$$P = \frac{N(T)\mu_p^2}{3K_B T} E + \frac{(1-f_{ex})(\epsilon_0 - 1)E}{4\pi} \quad (1)$$

where  $\mu_p$  is the dipole moment of a cluster and  $N(T)$  is the number of defect clusters at the absolute temperature  $T$ . The second term is due to the polarization of the defect-free background.

The dipole moment  $\mu_p$  can be estimated from the structure of a defect cluster as given by neutron scattering results (Hutchings *et al* 1984). For  $\text{PbF}_2$  with the smallest cluster (relative to  $\text{CaF}_2$  and  $\text{SrCl}_2$ )  $\mu_p$  comes out to be  $7.287 \times 10^{-17}$  esu.

The number of dipoles  $N(T)$  increases with temperature as more and more defect clusters are formed.  $N(T)$  is given by

$$N(T) = \frac{N_m}{N_c} f_{ex}(T). \quad (2)$$

Here  $N_m$  is the number of molecules per unit volume and  $N_c$  is the number of molecules in each defect cluster. So  $N_m/N_c$  is the maximum number of defect clusters that can be found per unit volume and  $f_{ex}(T)$  is the fraction of this number which actually contains a Frenkel pair.

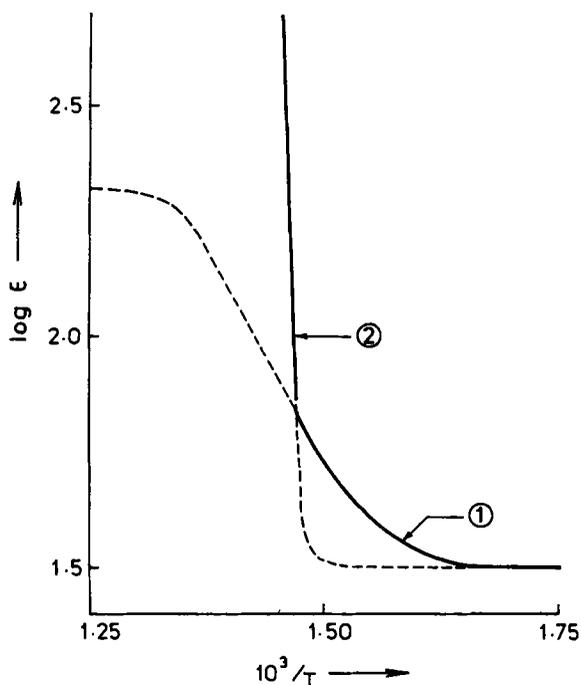
We have shown in Makur and Ghosh (1989) that the defect cluster can be regarded as an excited two-level-system. The excitation energy lies between the limits  $E_1$  and  $E_2$  with a constant density of states  $c$  and  $f_{ex}(T)$  has been estimated using parameters that fit different physical properties such as specific heat, thermal expansion and bulk modulus.

We proceed as in Makur and Ghosh (1989) to calculate  $f_{ex}(T)$ . Makur and Ghosh (1990) give respectively the specific heat *vs*  $T$  and ionic conductivity *vs*  $T$  curves for  $\text{PbF}_2$ . Best fit parameters are given in table 1. Now the susceptibility and hence dielectric constant for  $\text{PbF}_2$  is calculated from (1) using no additional parameter. The results are shown in figure 1.

As temperature rises, however, the number of defect clusters rises exponentially and inter-cluster interaction cannot be neglected. If we continue to neglect the interaction,  $P$  saturates as the number of defect clusters approaches the maximum number i.e.  $f_{ex}(T) \rightarrow 1$ . Experimental results do not show such behaviour, so we propose a different mechanism for high temperatures. The ionic conductivity can be qualitatively explained by assuming that the defect-cluster regions, where a local distortion of the lattice provides an easy path for motion of the anion vacancies (Makur and Ghosh 1989).

**Table 1.** Parameters used in  $\text{PbF}_2$ .

$E_1$ (ergs)	$E_2$ (ergs)	Cluster size $N_c$ in present model	Ionic conduction threshold, $T_{th}$		$c$ , density of states per erg
			Present model	expt.	
$3.07 \times 10^{-12}$	$3.30 \times 10^{-12}$	18	689.8 K	630 K	$4.25 \times 10^{26}$

**Figure 1.**  $\text{Log } \epsilon$  vs  $10^3/T$  for  $\text{PbF}_2$ : curves (1), (2) calculated from eqs (1) and (7).

When the temperature is low, defect clusters are isolated and there is no connected path for anion vacancies through the crystal, so the system is effectively an insulator. But at a certain temperature  $T_{th}$  the concentration of defect clusters reaches the percolation threshold and conduction starts. In Makur and Ghosh (1990)  $T_{th}$  for  $\text{PbF}_2$  has been determined as 689.8 K.

At a temperature  $T < T_{th}$  we visualize the crystal as a dielectric (with  $\epsilon \sim 32$  the room temperature value) in which a volume fraction  $f_{ex}$  is occupied by defect clusters.

As temperature rises, and hence  $f_{ex}$  increases there is a probability that two or more defect clusters are in adjacent positions. So a connected group of defect clusters is formed. We refer to this larger cluster comprising  $S$  defect clusters as an  $S$ -percolation cluster. At any given temperature the average percolation cluster size has a specified value  $\langle S \rangle_T$ . At the percolation threshold  $f_{ex}(c)$  where  $T = T_{th}$ ,  $\langle S \rangle_T$  diverges.

Now, we make a crucial assumption that as the anion vacancy can move relatively

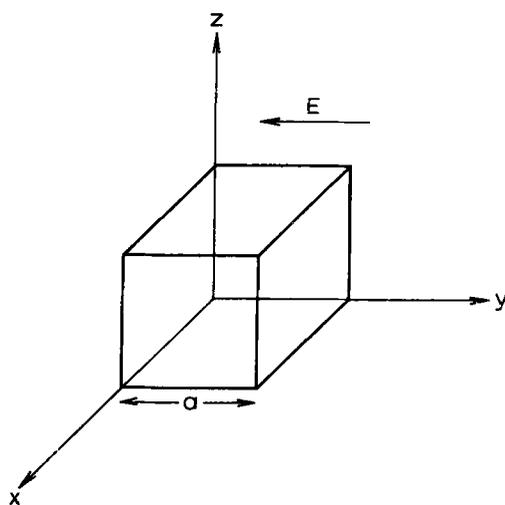


Figure 2. S-percolation cluster of  $\text{PbF}_2$  in an external electric field  $E$ .

easily through the defective region, the percolation cluster as a whole is polarized in the presence of an external electric field.

Figure 2 shows an S-percolation cluster (assumed to be cubic for simplicity) in the presence of a static electric field  $E$  along the  $y$ -direction.

The immobile interstitials are randomly distributed throughout the cluster volume  $a^3$ . The anion vacancies which are effectively positively charged move against the field.

At very low temperatures all the positive charges are thus located at the plane  $y = a$ . At a finite temperature, however, the vacancies tend to move towards the  $y = 0$  plane due to their thermal energy. In hopping from one site to another the anions have to overcome a potential barrier between sites. We neglect this barrier for the present and assume that positive charge density varies along the  $y$ -direction as

$$\rho^+ = \rho_0^+ e^{-(a-y)eE/K_B T} \quad (3)$$

If each defect cluster contains a single Frenkel pair, the total positive charge in the S-cluster is  $+Se$ .  $\rho_0^+$  can be determined from this condition to be

$$\rho_0^+ = \frac{S_e b}{a^2(1 - e^{-ba})} \quad (4)$$

where

$$b = \frac{eE}{K_B T}$$

The negative charge density, uniform throughout the S-cluster is given by

$$\rho^- = -Se/a^3 \quad (5)$$

We can now easily determine the dipole moment due to the S-cluster at a

temperature  $T$ . For not too large fields this is given by

$$\mu_s = \frac{Se^2 a^2}{4 K_B T} E \quad (6)$$

retaining terms up to  $b^2$  in the expansion of  $e^{-ba}$ .

The net dipole moment per unit volume is given by

$$P = N_d \mu_s + \frac{(1 - f_{ex})(\epsilon_0 - 1)}{4\pi} E. \quad (7)$$

$N_d$  = Number of dipoles per unit volume, i.e. number of  $S$ -clusters.

$$= \frac{N_m}{N_c} \cdot \frac{f_{ex}}{\langle S \rangle_T}$$

We disregard the distribution of cluster sizes and assume that all clusters are of the average size  $\langle S \rangle_T$  at a given temperature. Computer simulation studies of percolating systems (Stauffer 1979) give  $\langle S \rangle_T$  as

$$\langle S \rangle_T = \left[ \frac{f_{ex}(c) - f_{ex}(T)}{f_{ex}(C)} \right]^{-1.8} \quad (8)$$

The volume fraction  $f_{ex}(T)$  of the crystal which forms defect clusters is determined as in Makur and Ghosh 1989.

The susceptibility and hence dielectric constant are determined from (7). The calculated dielectric constant diverges at the temperature  $T_{th}$  where  $f_{ex} = f_{ex}(C)$  and ionic conduction starts. Different values of  $f_{ex}(C)$  ranging from 0.1–0.33 are obtained from experiments, computer simulation work and mean field theories. We have assumed  $f_{ex}(C) = 0.25$ .

It may be mentioned that (7) is not expected to give good results for  $f_{ex}$  far from  $f_{ex}(C)$ . The method of calculation of  $\mu_s$  is not suitable for very small  $S$  and (8) is also valid only close to  $f_{ex}(C)$ .

Figure 1 shows  $\log \epsilon$  plotted vs  $10^3/T$  for both expression (1) and (7).

The combined solid curve with curve (1) as the low temperature and curve (2) as the high temperature limits give  $\epsilon$  vs  $T$  as predicted by our model.

Experimental results for the static dielectric constant are not available, so it is not possible to compare the calculated result directly with experiment. But the frequency dependent conductivity measure by Kosacki and Zalibowski (1988) indicate that there should be a large increase in  $\epsilon$  as the temperature approaches  $T_c$ .

### 3. Discussion

The fit of our (Makur *et al* 1990 in figure 2(b)) calculated  $I_c$  vs  $T$  curve with the experimental result on  $PbF_2$  is rather unsatisfactory. Actually we have chosen the set of parameters which give an overall best fit for the specific heat, thermal expansion, bulk modulus and ionic conductivity. The threshold for ionic conduction  $f_{ex}(c)$  has been taken as 0.25 as for  $SrCl_2$  in Makur and Ghosh (1989), a lower value would give a somewhat better fit.

A direct comparison of the experimental results of Kosacki and Zalibowski (1988) with our calculations is not very meaningful. This is because the low frequency limit of the experimental result should give the static dielectric constant, but at low frequencies the measured  $\epsilon$  may not be reliable. It is not clear whether the capacitance measured in Kosacki and Zalibowski (1988) has been corrected for the capacitance due to the charge depletion layers formed at the surface of the sample. At the frequencies used, such capacitances are likely to be comparable to the bulk capacitance at high temperatures, as discussed by Oberschmidt and Lazarus (1980) and in that case corrected capacitances would be much higher.

We thus consider the present model to give a plausible qualitative description of the temperature dependence of the dielectric constant of  $\text{PbF}_2$ . However more experimental work is required, before more definite conclusions can be drawn about the dielectric behaviour of superionic fluorites.

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