

RETARDED IONIC MOTION IN FLUORITES

J. SCHOONMAN

*Solid State Department, Physics Laboratory, State University,
3508 TA Utrecht, The Netherlands*

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Metal halides with the fluorite structure attain conductivity values typical of ionic melts far below their melting points, and also go through a second-order transition. Conductivity data for the fluorites are reviewed, and it is shown that the anion vacancies have a large and unique mobility value at the transition temperatures T_c . At T_c only small concentrations of defects are present, which strongly contradicts the concept of anion-sublattice melting. The conductivity mechanism above T_c is discussed in relation with the enhanced ionic motion model developed for concentrated anion-excess solid solutions based upon fluorites. As a consequence of unusually large defect mobilities at T_c it is noted that retard ionic motion occurs above T_c .

1. Introduction

A number of materials with the fluorite structure, notably CaF_2 , SrF_2 , BaF_2 , SrCl_2 and $\beta\text{-PbF}_2$, attain high values of anionic conductivity, and also go through a diffuse or second-order transition [1–9]. Characteristic of these fluorites is the occurrence of a negative deviation from the Arrhenius relation on going through this so-called Faraday transition [8]. Derrington et al. [6], Dworkin and Bredig [10], and Belosludov et al. [11] found broad specific heat anomalies in these fluorites at temperatures T_λ (specific heat maximum) well below the melting temperatures, and equal or below the temperature T_c where the negative deviation from the Arrhenius relation occurs. It is assumed that the broad specific heat anomaly and the high value of ionic conductivity are associated with a gradual development of massive disorder in the array of the conducting halide ions: the concept of a molten sublattice.

Although neutron scattering experiments reveal increasing anharmonicity and displacements of the ions, the extent of anti-Frenkel disorder above T_c has not been settled firmly. Estimates of halide interstitial concentrations obtained by this approach vary from 20% in SrF_2 at about 1550 K [12] to about 40% in BaF_2 and $\beta\text{-PbF}_2$ near their melting point [13], while light scattering data for $\beta\text{-PbF}_2$ lead to estimates of 16% at 775 K ($\approx T_c$) and 28% at 881 K [14]. In contrast to these large defect concentrations Dickens et al. [15] concluded from their neutron diffraction experiments on SrCl_2 that only 3% of chloride interstitials are present at 1093 K,

i.e. well above T_c (1000 K). Theoretical computations which also account for lattice anharmonicity [16], lead to 10% halide interstitials in fluorites around T_c .

Detailed conductivity studies on $\beta\text{-PbF}_2$ and SrCl_2 [9] reveal above T_c conductivity activation enthalpies of about 0.2 and 0.3 eV, respectively. These values are comparable to the anion vacancy migration enthalpies as measured in the extrinsic conductivity region. Carr et al. [9] arrive, on using a theoretically predicted almost temperature-independent anti-Frenkel defect concentration [16], at the assumption that simple anion vacancy conduction predominates at temperatures above the Faraday transition. A Haven ratio between 0.7 and 1.0 [9, 17] at these high temperatures provides added emphasis, since this ratio range is usually found for conduction mechanisms involving isolated point defects in dilute materials.

This simple mechanism is in contrast to the observation that the temperature dependence of the ^{19}F spin-lattice relaxation rate in $\beta\text{-PbF}_2$ does no longer obey the usual random walk expression in this high-temperature region. Fluoride ion motion is predicted to be highly correlated as a consequence of a high degree of disorder [7]. Recent molecular dynamics simulations of ionic conductivity in SrCl_2 [18] and CaF_2 [19] contradict the idea that the anion sublattice is liquid-like at temperatures above the Faraday transition. The question as to whether cooperative modes of motion in a liquid-like sublattice rather than isolated jumps with a small extent of disorder are involved at high temperatures seems therefore, still open to discussion.

A large number of conductivity studies on these fluorites have appeared in the recent literature. These studies were performed in broad temperature regions, and provide information on defect concentrations and defect mobilities up to T_c , which is interesting since T_c approximately equals T_λ . None of the studies to date has taken full advantage of the available conductivity data for dilute fluorites, neither has recent structural information been employed in establishing a high-temperature conductivity mechanism.

It will be shown that the onset of the Faraday transition is accompanied by a striking similarity between these fluorites. Moreover, the defect data raise several questions as to the reported extent of disorder and the conduction mechanism at temperatures above the Faraday transition. It will further be shown that anion-sublattice melting is definitely not required to account for the high-temperature conductivity of fluorites, and that even retarded ionic motion occurs above T_c .

2. Defect parameters

For the alkaline earth fluorides and $\beta\text{-PbF}_2$ the literature provides detailed information on defect mobilities and defect concentrations. For SrCl_2 sufficient data are available to obtain a relation for the temperature dependence of the chloride ion vacancy mobility. Before presenting numerical data some comments are in order, since not all available data will be used in detail here.

2.1. CaF_2

Ure [20] reported the mobility of fluoride interstitials in CaF_2 , while Bollmann and co-workers [21,22] obtained the mobility of the fluoride ion vacancies, and fluoride interstitials, as well as the concentrations of the thermally generated anti-Frenkel defects. The data of Ure revealed the rather high value of 1.6 ± 0.3 eV for the migration enthalpy of the fluoride interstitials. Bollmann and Reimann reported the value 0.92 eV [22]. Ure indicated that his analysis of the conductivity data could lead to substantial errors in the values for the interstitial mobility, since a correction had to be made for conduction of fluoride interstitials along grain boundaries. A detailed study and analysis of the conductivity of CaF_2 appeared more recently, and revealed numerical values for defect parameters that are consistent with the data reported by Bollmann and co-workers [23].

2.2. SrF_2

The ionic conductivity of SrF_2 has been studied by Barsis and Taylor [24] and by Bollmann et al. [25], the latter authors reporting the only numerical values for the mobilities and concentrations. They observed a constant ratio between the mobility of the interstitial and that of the vacancy at all temperatures, i.e. $\mu_{\text{F}_i}/\mu_{\text{V}_\text{F}} = 4.13$, while the data of Barsis and Taylor [24] clearly indicate $\mu_{\text{V}_\text{F}} > \mu_{\text{F}_i}$ at low and moderate temperatures. More recently, Chadwick et al. [26] showed the vacancy mechanism indeed to be predominant in undoped SrF_2 .

2.3. BaF_2

For BaF_2 considerable discrepancies are found in the reported values for the fluoride ion vacancy mobility [27,28]. Recently, Carr et al. [29] and Figueroa et al. [30] studied the ionic conductivity and self-diffusion in BaF_2 . These studies led to activation enthalpies that are consistent with the data for fluoride ion vacancies reported by Barsis and Taylor [27]. The literature data for the interstitial mobilities are reasonably consistent.

2.4. $\beta\text{-PbF}_2$

The ionic conductivity of $\beta\text{-PbF}_2$ has been reviewed recently by Bonne and Schoonman [31]. They obtained the temperature dependence of the mobility of the fluoride ion vacancies and fluoride interstitials taking into account the available literature data.

2.5. SrCl_2

The ionic conductivity of nominally pure and doped SrCl_2 has been studied by

several authors [24, 32, 33]. Consistent values for the conductivity activation enthalpies were obtained. All data for doped materials revealed substantial association of oppositely charged defects at low and moderate temperatures. Gervais et al. [32] interpreted all extrinsic conductivities using the Debye–Hückel–Lidiard theory and arrived at a reasonably consistent set of data for the migration enthalpy and entropy of chloride ion vacancies in SrCl_2 . For the attempt frequency ν_0 , which appears in the pre-exponential factor of the mobility relation, they have used the value $5.22 \times 10^{12} \text{ s}^{-1}$ [34] which appears to be close to the frequency of a Raman active mode [35]. For the fluorides the numerical data for the pre-exponential factors in the mobility relation lead to attempt frequencies that are concordant with reported transverse optic frequencies [22, 25, 31, 35, 36]. For SrCl_2 this frequency has the value $4.44 \times 10^{12} \text{ s}^{-1}$, and this value should be considered in a further analysis of the pre-exponential factor. The data of Gervais et al. [32] lead to the following relation for the chloride ion vacancies

$$\mu_{\text{V}_{\text{Cl}}} = (1.4 \times 10^2 / T) \exp(-0.336 \text{ eV} / kT) \text{ cm}^2 / \text{V s}. \quad (1)$$

The mobility data of Barsis and Taylor [24] lead to an attempt frequency which is too large by a factor of about 3. Their study included only a few extrinsic conductivities, and was mainly focused on establishing the intrinsic conductivity region of SrCl_2 .

3. Defect parameters at T_c

In figs. 1 and 2 we have presented literature data for the mobility of the anion vacancies and anion interstitials, respectively. It should be stressed that for temperatures greater than T_c the figures only present extrapolated mobility data that may not have physical meaning. The temperature dependence of the intrinsic defect concentrations is given in fig. 3. Table 1 [21, 22, 25, 27, 28, 31] presents the concentrations of the intrinsic anti-Frenkel defects in mole per cent (m/o), the defect mobilities, and the partial ionic conductivities at the temperatures T_c where the negative deviation from the Arrhenius relation occurs. Data for $\mu_{\text{V}_{\text{F}}}$ in SrF_2 were not included in fig. 1 and table 1, since the data reported by Bollmann et al. [25] are most probably in error.

The data in fig. 1 indicate that the occurrence of a negative deviation from Arrhenius behavior is related with a critical mobility for the anion vacancies. The data in table 1 show its value to be about $2.6 \times 10^{-3} \text{ cm}^2 / \text{V s}$, while T_c values are found in the range 780–1450 K. A critical mobility is less apparent for the halide interstitials.

At low and moderate temperatures the condition $\mu_{\text{V}_{\text{F}}} \gg \mu_{\text{F}_i}$ holds for fluorites, whereas at T_c $\mu_{\text{F}_i} > \mu_{\text{V}_{\text{F}}}$ holds. One expects, therefore, a positive deviation from the Arrhenius relation to occur in fluorites below T_c . Such deviation has indeed

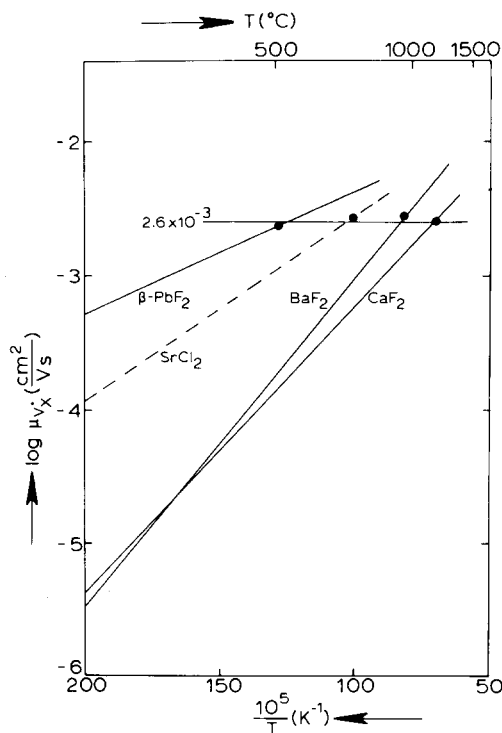


Fig. 1

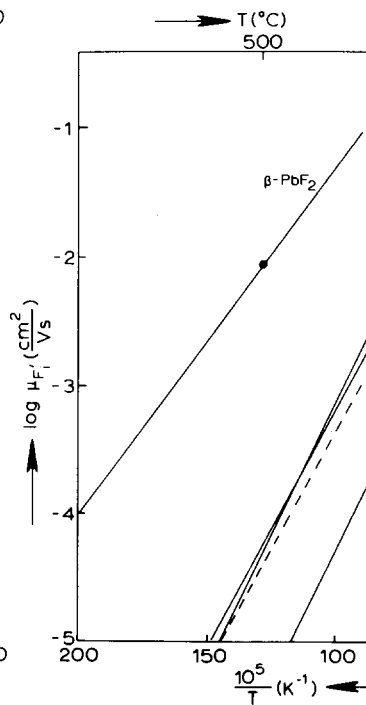


Fig. 2

Fig. 1. The temperature dependence of the mobility of the anion vacancies in CaF_2 [21], [27], $\beta\text{-PbF}_2$ [31] and SrCl_2 [eq. (1)]. T_c is indicated by •.

Fig. 2. The temperature dependence of the mobility of the anion interstitials in CaF_2 [22], SrF_2 [25], BaF_2 (— [28], --- [27]), and $\beta\text{-PbF}_2$ [31]. T_c is indicated by •.

been observed for SrF_2 [38] and BaF_2 [29,38] starting about 400 K below T for $\beta\text{-PbF}_2$ starting at about 240 K below T_c [7,17,31]. The upward curvature often been related with the broad specific heat anomaly, and hence the onset of ordering of the anion sublattice. Boyce et al. [7] attribute, for instance, the positive deviation to interactions between the vacancies and the interstitials, which can allow more defects to be generated than is predicted by the Arrhenius relation. The concentration for this interaction to be important is according to Hubermann about 1 m/o [39]. Considerably smaller concentrations are present in $\beta\text{-PbF}_2$ and the alkaline earth fluorides several hundreds of degrees below T_c as can be inferred from table 1 and fig. 3. Instead it has now been shown convincingly that this positive deviation relates to a change from intrinsic conductivity by fluoride ion vacancies to intrinsic conductivity by fluoride interstitials [29–31,37,40]. It should, however, be pointed out that Carr et al. [29] found evidence for slightly higher conduc-

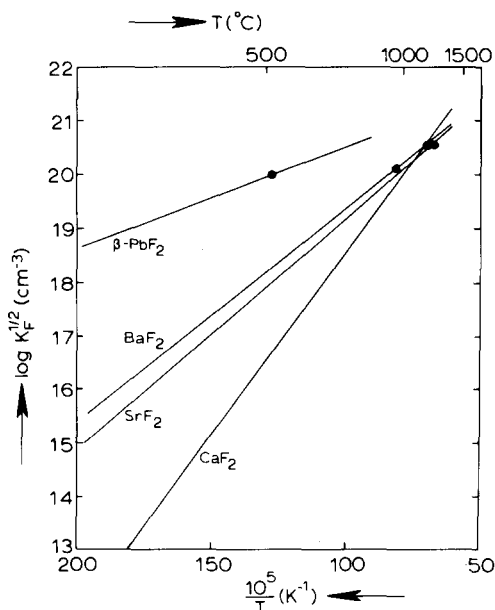


Fig. 3. The temperature dependence of the concentrations of the intrinsic point defects ($K_F^{1/2} = [F_i^{\bullet}] = [V_F]$) in alkaline earth fluorides, and β - PbF_2 [31]. T_c is indicated by \bullet .

ties in the region 1120–1250 K ($= T_c$) than can be modelled with the vacancy to interstitial conductivity change over. From the concentration data in table 1 it is apparent that vacancy–interstitial interactions [39] can be of importance around T_c , and the cause of this deviation in the region 1120–1250 K.

4. Discussion

The high ionic conductivity of fluorites has in general been related to massive disorder, and not to high defect mobilities. From the data in table 1 it is, however, apparent that the fluorites already exhibit conductivities of the order of molten salts at T_c , and that this is more due to high defect mobilities than to a large extent of disorder. Inspection of table 1 reveals that at T_c the defect concentrations are found in the range ≈ 0.5 to ≈ 2 m/o, and that both halide ion vacancies and halide interstitials contribute to the conductivity. That the interstitials constitute the more mobile species around T_c , casts doubt on the vacancy-mechanism proposed by Carr et al. [9] for the high-temperature conductivity of at least β - PbF_2 .

It has been proposed that the high-temperature conductivity of the fluorites is a consequence of considerable anharmonicity [41,42]. The effects of dynamic and

Table 1
The concentrations, mobilities and partial conductivities in fluorites at T_c . T_λ represents the temperature of the specific heat maximum

Fluorite	T_λ (K) a)	T_c (K)	$K_F^{1/2}$ (T_c) (m/o)	μV_F (T_c) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μF_i (T_c) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	σV_F (T_c) ($\Omega^{-1} \text{cm}^{-1}$)	σF_i (T_c) ($\Omega^{-1} \text{cm}^{-1}$)
CaF ₂	1430 [10]	1450 [4, 5]	1.45	2.63×10^{-3}	1.48×10^{-2}	1.49×10^{-1}	8.41×10^{-1}
SrF ₂	1400 [11]	1480 [4]	1.92		1.22×10^{-3}		7.61×10^{-2}
BaF ₂	1230 [11]	1250 [5]	0.94	2.94×10^{-3}	3.98×10^{-3}	7.45×10^{-2}	1.0×10^{-1}
β -PbF ₂	705 [6]	780 [31, 37]	0.52	2.34×10^{-3}	8.71×10^{-3}	3.74×10^{-2}	1.39×10^{-1}
SrCl ₂	1000 [10]	1000 [5]		2.87×10^{-3}			

a) Numbers in brackets refer to text references.

static displacements on the elastic neutron scattering diffraction pattern are, however, indistinguishable. The inelastic neutron scattering experiments [41] show, as do the light scattering data [14], that the Raman active mode becomes unobservable in SrCl_2 and $\beta\text{-PbF}_2$ as a discrete mode around T_c , and for temperatures larger than T_c . For $\beta\text{-PbF}_2$ this observation has led to an estimate of 16% of interstitials at 775 K ($\approx T_c$) [14]. Recent neutron diffraction studies [43] indicate that in $\beta\text{-PbF}_2$ from 600 to 900 K 5–40% of fluoride ions leave their regular sites, and that in SrCl_2 from 900 to 1100 K about 0.5–3% of chloride ions leave their regular sites. Schulz and Koto [44] observed in high-temperature X-ray studies on $\beta\text{-PbF}_2$ single crystals that for $T > 730$ K, i.e. in between T_λ and T_c , fluoride ions are displaced toward the faces of the tetrahedrons formed by lead ions. In BaF_2 as many as 20% of the fluoride ions are displaced due to anharmonic thermal vibrations [42]. Although these recent findings confirm the earlier data [12,13] it is apparent from the concentration data in table 1 that these displaced ions are by no means representative of the actual number of conducting ions, and that in doing so unrealistically large interstitial concentrations are obtained [14]. In regard of the large amounts of displaced lattice halide ions, the small number of actually conducting defects, and a critical vacancy mobility at T_c it is interesting to note that several authors have claimed a (displacive) first-order transition to occur in fluorites. Although rather unusual for inorganic solids in general, the cubic α -form of CaF_2 transforms to a less symmetric tetragonal form at 1424 K, i.e. at T_λ [45,46], while at 1002 K a first-order transition has been observed in SrCl_2 [47]. For $\beta\text{-PbF}_2$ a third form ($\gamma\text{-PbF}_2$) has been reported by Banashek et al. [48] for temperatures around the specific heat anomaly.

The displaced ions might play an important role in the conduction mechanism for temperatures larger than T_c . For the small conducting defect concentrations, and the condition $\sigma(\text{F}_i^+) > \sigma(\text{V}_\text{F}^-)$ at T_c , we can postulate a similar situation to occur as encountered in the low-temperature conductivity of concentrated anion-excess solid solutions based upon fluorites [49]. In these solid solutions the anion-excess is mainly present in defect clusters with strongly distorted areas around them. Only a small fraction of interstitials, i.e. about 0.3 m/o [49], does carry the current via the non-collinear interstitialcy mechanism. Since the displaced lattice ions around the clusters are involved in this mechanism the activation enthalpy for conduction is much lower than in the undisturbed lattice. A similar situation then occurs in the nominally pure fluorites beyond the Faraday transition, i.e. reduced activation enthalpies if the displaced lattice ions are involved in the non-collinear interstitialcy mechanism. That the conductivity activation enthalpy for $T > T_c$ is larger if the number of displaced ions decreases, as is found for SrCl_2 compared to $\beta\text{-PbF}_2$, is a further indication for this mechanism. For the usual vacancy mechanism this reduction of activation enthalpy can be anticipated as well, although it must be noted that the physical meaning of a critical anion vacancy mobility in fluorites at T_c is presently unclear.

There remains, however, one important difference to note. In the anion-excess

solid solutions the displaced ions lead to strongly enhanced ionic motion for interstitials (EIM model [49]), while it appears that the conduction mechanism for $T > T_c$ produces lower rather than higher values of the conductivity than would be present if the mechanism below T_c , also used as the reference state in the EIM model, were to persist above T_c [50]. O'Keeffe [2] has discussed the absolute magnitude of the diffusion coefficient in solid electrolytes. A comparison between diffusion coefficients in solids and liquids points to an upper limit of about 10^{-4} cm²/s in solids, and thus to an upper limit for the mobility. Putting for convenience T_c values in the Einstein relation leads to the value 8×10^{-3} cm²/V s as the upper limit for defect mobilities in CaF₂, 9.3×10^{-3} cm²/V s for BaF₂, and 1.5×10^{-2} cm²/V s for β -PbF₂. The mobility data in table 1 reveal the interstitial mobility in CaF₂ to be larger than the "limiting" value, while for BaF₂ and β -PbF₂ the interstitial mobilities approach the limiting values. In these situations a negative deviation from the Arrhenius plot of mobilities can be expected to start at about T_c .

From conductivity data, for comparison, we obtain for undoped BaF₂ and for Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231} at 473 K for the interstitial mobility the value 3.80×10^{-8} and 5.75×10^{-5} cm²/V s, respectively, thus illustrating enhanced ionic motion [51], but also that these values are much smaller than the "limiting" values. In the nominally pure fluorites the lowering of the activation enthalpy starts as a consequence of the small structural changes around T_c , but this does not lead — as in the solid solutions — to enhanced ionic motion, since the defect mobilities are already of the order of the "limiting" values at T_c .

At high temperatures the fluorites are often referred to as superionic conductors [18,38,52], or solids that exhibit fast ionic conduction [43]. That these terms are misnomers [5], or at least can be misleading [50] has recently been stressed. In light of the present discussion, and despite the high mobility values at T_c , one can argue that the use of the term "retarded ionic motion" is more appropriate in describing the high-temperature conductivity of the fluorites.

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