

Migration parameters of the bound fluorine in trivalent-cation-doped BaF₂

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The ratio of the migration entropy s over the migration enthalpy h of the bound fluorine in trivalent-cation-doped BaF₂ is estimated with different experimental methods. A thermodynamical model proposed by Varotsos and Alexopoulos is used in order to correlate the ratio s/h with the macroscopic quantities of the host crystal (bulk modulus and thermal-expansion coefficient). This model seems not to be valid in general. We point out that there are deviations for dopants with large ionic radii. In this case, we speculate that the usual arbitrarily chosen attempt frequency of the bound fluorine which leads to the evaluation of s is incorrect.

INTRODUCTION

Some years ago Varotsos and Alexopoulos¹⁻³ formulated the $cB\Omega$ model which states that the enthalpy h and the entropy s corresponding to a defect process (formation, migration, or activation) in materials, are interconnected with the bulk properties of the host crystal according to the following relation:

$$\frac{s}{h} = - \frac{\beta B - (\partial B / \partial T)_p}{B - T\beta B - T(\partial B / \partial T)_p}, \quad (1)$$

where β is the thermal-expansion coefficient and B the isothermal bulk modulus of the host material. The ratio s/h is defined from the macroscopic quantities of the host material and, for a given crystal, is the same for different impurities introduced in it.

EXPERIMENTAL ESTIMATION OF THE RATIO s/h

In rare-earth-doped alkaline-earth fluorides the substituting cation may form NN or NNN dipoles with the interstitial fluorine anions. In trivalent cation doped BaF₂ the NNN dipoles are the dominant ones. ITC experiments on the above crystal detect a strong peak around 195 K that is attributed by all the authors⁴⁻¹² to NNN dipole relaxation corresponding to the motion of the NNN-bound fluorine interstitial between equivalent sites. This process is determined by two energy parameters:

The migration enthalpy of the bound fluorine h and the preexponential factor τ_0 of a usual Arrhenius relation:

$$\tau = \tau_0 \exp \left[\frac{h}{kT} \right], \quad (2)$$

where k is the Boltzmann constant and τ denotes the relaxation time. The migration entropy s is given by²

$$s = k \ln \left[\frac{\tau_0^{-1}}{\lambda \nu} \right], \quad (3)$$

where ν is the frequency of the vibrating ion towards the potential barrier and λ is the number of the jump paths accessible to the (moving) ion with attempt frequency ν . This frequency is arbitrarily taken equal to the frequency ν_{TO} of the long-wavelength transverse optical mode, while, for jumps via NNN paths, we may set $\lambda=2$. Since $\nu_{\text{LO}} \approx 2\nu_{\text{TO}}$ then Eq. (3) is written

$$s = k \ln \left[\frac{\tau_0^{-1}}{\nu_{\text{LO}}} \right]. \quad (4)$$

The preexponential factor τ_0 and the migration enthalpy h are estimated from ITC, thermally stimulated polarization currents (TSPC), or dielectric relaxation experiments. The mean value of ν_{LO} around 195 K was extracted by interpolating and extrapolating the data reported by Lowndess,¹³ Bosomworth,¹⁴ and Denham *et al.*¹⁵ and

TABLE I. The ratio s/h evaluated from the experimental data (Ref. 9) for different impurities. The ionic radii R are taken from Refs. 20 and 21.

Impurity	R (Å)	h (eV)	τ_0 (10^{-14} sec)	s (k)	s/h (10^{-4} K ⁻¹)
Ce ³⁺	1.28	0.619	1.3	2.034	2.83
Pr ³⁺	1.28	0.617	2.6	1.341	1.87
Nd ³⁺	1.26	0.693	0.053	5.234	6.51
Sm ³⁺	1.23	0.692	0.086	4.750	5.92
Gd ³⁺	1.20	0.635	0.92	2.380	3.23
Y ³⁺	1.16	0.561	3.3	1.102	1.69
Ho ³⁺	1.16	0.595	0.72	2.625	3.80
Tm ³⁺	1.13	0.540	1.4	1.960	3.13

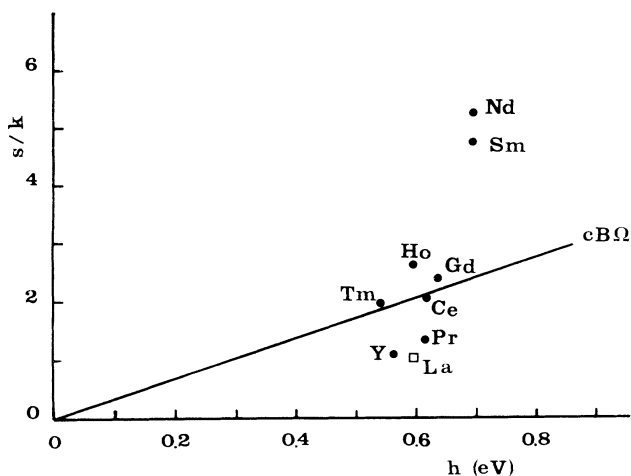


FIG. 1. The migration entropy s vs the migration enthalpy h of the bound interstitial fluorine: ●: for different impurities from Laredo *et al.*⁹ Notice that the impurities with small ionic radii are in accordance with the $cB\Omega$ model. □: for La^{3+} from Wapenaar *et al.*⁶ —: according to the $cB\Omega$ model.

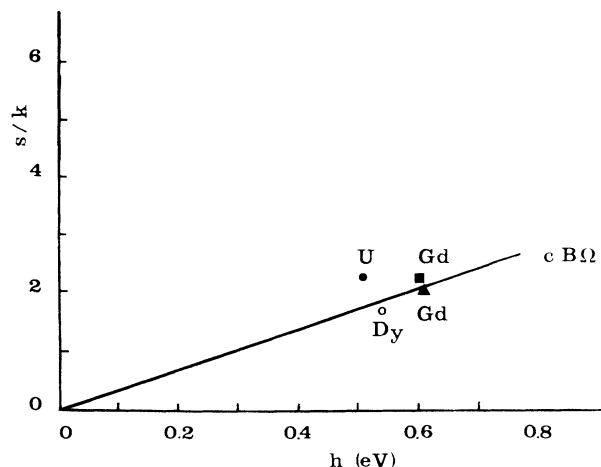


FIG. 2. The migration entropy s vs the migration enthalpy h of the bound interstitial fluorine from several researchers and for various impurities. —: $cB\Omega$ model, ○: Dy^{3+} (Ref. 4); ●: U^{3+} (Ref. 5); ▲: Gd^{3+} (Ref. 7); ■: Gd^{3+} (Ref. 8).

is approximately equal to $1.006 \times 10^{13} \text{ sec}^{-1}$. Subsequently, the migration entropy s is calculated inserting the experimental data into Eq. (4) for different impurities and then the ratio s/h is evaluated.

EVALUATION OF THE RATIO s/h FROM THE $cB\Omega$ MODEL

The right side of Eq. (1) is calculated using the values of B and dB/dT was extracted from the elastic data from Wong and Schuele¹⁶ and the value of β from Bailey and Yates,¹⁷ Roberts and White,¹⁸ and White.¹⁹ At $T=195$ K we have:

$$B = 0.59 \times 10^{11} \text{ N m}^{-2},$$

$$dB/dT = 2.1122 \times 10^7 \text{ N m}^{-2} \text{ K}^{-1}$$

$$\beta = 4.7778 \times 10^{-5} \text{ K}^{-1}.$$

Substituting into Eq. (1) we get:

$$s/h = 2.93 \times 10^{-4} \text{ K}^{-1}.$$

In a s -vs- h diagram the $cB\Omega$ prediction is represented by a straight line (solid line in Figures 1 and 2) with slope equal to $2.93 \times 10^{-4} \text{ K}^{-1}$.

EXPERIMENTAL RESULTS

Laredo *et al.*¹¹ have reported ITC results on BaF_2 doped with a large variety of impurities concerning the NNN dipoles. Their data were interpreted both with a monoenergetic model and a Gaussian-distributed-energy model. The first one leads to negative migration entropies. The latter permits the evaluation of positive migration entropies (Table I). In this case, in an s -vs- h diagram (Fig. 1) the experimentally determined points according to Table I scatter around the theoretical prediction ($cB\Omega$ model).

This scattering does not seem random. Most of the rare-earth ions having ionic radii smaller than about 1.22 \AA are close to the $cB\Omega$ model, while most of those having ionic radii larger than about 1.22 \AA show considerable deviations. (The ionic radii were taken from Refs. 20 and 21.) The data for La^{3+} (from Ref. 11) have been omitted from Table I and Figure 1 since the corresponding migration entropy is negative.

Recent experimental data^{4,5} for the orientation of NNN dipoles are shown at Table II and Fig. 2 together with the results from two previously published papers.^{7,8} These data agree satisfactorily with Eq. (1), represented in Fig. 2 by a solid line. Notice that the U^{4+} ions reduce

TABLE II. The ratio s/h for several impurities published by different authors. The ionic radii are from Refs. 20 and 21.

Impurity	R (\AA)	h (eV)	τ_0 (10^{-14} sec)	s (k)	s/h (10^{-4} K^{-1})	Ref.
Dy^{3+}	1.17	0.537	1.995	1.605	2.58	4
U^{3+}	1.30	0.508	1.000	2.296	3.89	5
Gd^{3+}	1.20	0.61	1.224	2.094	2.96	7
Gd^{3+}	1.20	0.60	1.000	2.297	3.30	8

to U^{3+} ions when they are introduced into the BaF_2 crystals, so they form $U^{3+}-F^-$ dipoles.⁵ We stress that Gd^{3+} and Dy^{3+} have small ionic radii. Uranium that has a larger ionic radius deviates relatively more.

It is worth noticing that the relaxation parameters for $BaF_2:La^{3+}$ reported up to date by different authors^{5,10,11} lead to negative migration entropies. The only exception is that of Wapenaar *et al.*⁶ whose evaluated migration entropy deviates from the $cB\Omega$ prediction (Fig. 1). The migration entropy is also negative for the $BaF_2:Tb^{3+}$ system.¹² We stress that the ionic radius of La^{3+} is the largest one ($R = 1.32 \text{ \AA}$).

CONCLUSION

We conclude that the experimental data for BaF_2 doped with impurities having small ionic radius fit well to the $cB\Omega$ model. For dopants with large ionic radius, considerable deviations exist.

In order to clarify this aspect we have to trace back to Eq. (1). Apart from the experimental errors in determining the preexponential factor τ_0 , the migration entropy s depends upon the frequency ν which is arbitrarily chosen equal to ν_{TO} . We speculate that this assumption is not valid for impurities with large ionic radius.

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