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Fluorine Self-Diffusion in CaF_2 and BaF_2

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The self-diffusion of F-18 in single crystals of BaF_2 and CaF_2 was measured between 350 and 940°C. The results were in agreement with diffusion coefficients deduced from ionic conductivity studies, and yielded ΔH's of 1.6 eV for BaF_2 and of 2.0 eV for CaF_2 for intrinsic diffusion. Below 700°C, extrinsic diffusion behaviour was observed in CaF_2 with $\Delta H =$ 0.9 eV. The formation energy for anion Frenkel defects was estimated to be in the range 2.2 to 3.1 eV. Both anion and cation diffusion rates were increased in CaF_2 doped with SmF_3 as compared with pure CaF_2, indicating an interrelation between anion and cation defects, as observed previously in the related substances, UO_2 and UO_{2+x}. The migration energy of cations was estimated to be roughly in the range 1.5 ± 0.6 eV. The implications of the results in terms of diffusion mechanisms are discussed and the remaining uncertainties are indicated.

1. Introduction

The motion of fluorine ions in CaF_2 and BaF_2 has so far been examined by means of ionic-conductivity measurements [1-4]. Direct tracer-diffusion data are not available for BaF_2 and a few preliminary results [5] only have been reported for CaF_2. The probable reason for this lack of data is the inconveniently short half-life of the only useful tracer for fluorine, F-18, of 1.7 h. The present paper gives experimental results on the diffusion of F-18 in single crystals of BaF_2 and CaF_2 within broad temperature ranges of 350 to 940°C for CaF_2 and 435 to 900°C for BaF_2. In addition, some data are presented on cation diffusion in CaF_2. The combined results give some further insight into the defect structure of CaF_2.

2. Experimental

Single crystals (Harshaw, Cleveland, Ohio) with optically polished faces were pre-annealed in high vacuum and then covered with a *thin layer* of BaF_2 or CaF_2 containing radioactive F-18. The latter was obtained by reactor irradiation of $LiNO_3$ and chemical separation [6, part I; 7].

Diffusion-anneals were performed in high vacuum (approx. 10^{-6} torr) or in purified and dried argon. Since the results obtained for these two annealing conditions were in good agreement, no further reference will be made to the annealing conditions. Following some preliminary experiments and at temperatures above 700°C, two crystals were always annealed as a diffusion couple with the active layers sandwiched between the two crystals in order to prevent excessive evaporation. Following annealing, concentration profiles were obtained by conventional sectioning techniques using grade 600 emery paper and counting the radio-activity remaining in the crystal, using the 0.51 MeV annihilation γ-line of F-18. For details, see part I, reference 6.

3. Theoretical

The solution of the diffusion equation appropriate for most experiments is a simple error function since the applied active layer is thin and the absorption of the 0.51 MeV γ-radiation in the specimen can be neglected:

$$C/C_0 = \mathrm{erfc}\,(\tau) \qquad (1)$$

where $\tau = x/2\sqrt{Dt}$; C_0 = total initial concentration of the tracer isotope; C = remaining concentration of the tracer isotope following removal of a layer of thickness, x; D = diffusion coefficient in cm²/sec; t = annealing time in sec.

4. Results

Some typical concentration profiles are shown in fig. 1. Usually, the experimental points could

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*Experiments performed in 1968 at CCR Euratom, Ispra, Italy. The present study constitutes part II of a study of fluorine self-diffusion. Part I is concerned with LiF and NaF (see ref. [6]).

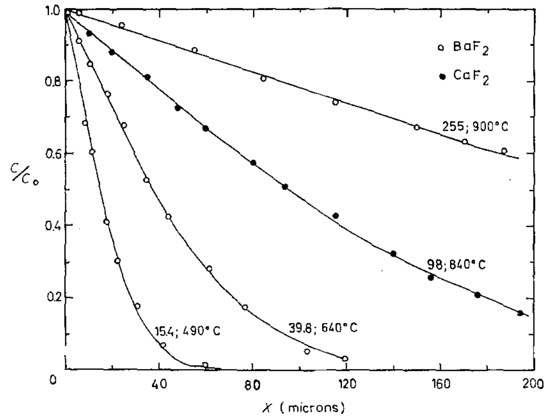

Figure 1 Concentration profiles for diffusion of F-18 in CaF_2 and BaF_2 single crystals. The experimental points have been fitted to curves as described by equation 1. The numbers at the curves represent the corresponding values of $10^4 \times \sqrt{Dt}$ and the experimental temperatures.

well be fitted to curves as described by equation 1, except in some preliminary runs where temperatures above 700°C and one sample only were used. In these experiments, losses of F-18 due to evaporation occurred. The resulting concentration profiles could be fitted to curves as described by the mathematics given in reference 8. However, all these measurements were repeated using diffusion couples, thus avoiding evaporation losses. Only these latter runs were plotted in the Arrhenius diagram of fig. 2. The data for BaF_2 could be fitted to one single line. A least square analysis yielded an activation enthalpy, ΔH, of 36.8 $\pm$ 3.5 kcal/mole (1.60 $\pm$ 0.15 eV/atom) and a pre-exponential term, D_0, of 3.1 cm^2 sec^{-1} ($\log D_0 = 0.49 \pm 0.12$). This line practically coincided with the one calculated from the conductivity data of Barsis and Taylor [2]. To perform this calculation, and the ones for CaF_2 (see below), the applicability of the Nernst-Einstein relation was assumed. The corresponding diffusion constants of Barsis and Taylor are 1.64 $\pm$ 0.03 eV and 6.2 cm^2 sec^{-1}.

The Arrhenius plot for CaF_2 clearly shows a break (or knee) at around 700°C. No least-square analysis was performed for these data because of the difficulty of determining the exact position of the knee. The diffusion parameters were $\Delta H \approx 46.5$ kcal/mole (≈ 2.0 eV), $D_0 \approx 50$ cm^2 sec^{-1} above 700°C, and $\Delta H \approx 21$ kcal/mole (≈ 0.9 eV), $D_0 \approx 10^{-4}$ cm^2 sec^{-1} below 700°C. A knee was observed in the conductivity data of Ure [1] and of Barsis and Taylor [2] as well though at slightly lower temperatures as indicated in fig. 2 by the dashed lines. The diffusion parameters deduced from the conductivity data are included in Table I. Fluorine diffusion is seen to be increased (experiment at 700°C, indicated by a triangle) in a CaF_2 single crystal doped with nominally 0.24 mol % Sm. This crystal was of green colour and hence contained both Sm^{3+}- and Sm^{2+}-ions (e.g. references 15-17). This colour did not change during annealing indicating that no oxidation took place during the diffusion anneal.

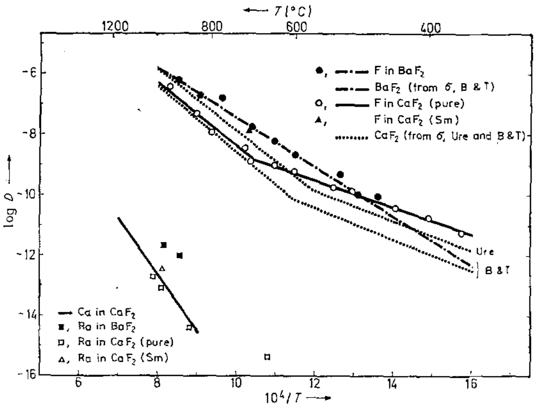

Figure 2 Arrhenius diagram for the diffusion of F-18 in CaF_2 and BaF_2 single crystals. Literature data on ionic conductivity were transformed into diffusion data assuming the applicability of the Nernst-Einstein relation (dashed curves, references 1, 2). For comparison, the literature data [13] for diffusion of Ca45 in CaF_2 are represented by the straight full line in the left hand corner together with some new data on the diffusion of Ra-224 in CaF_2 and BaF_2 single crystals. The two triangles represent results for diffusion of F-18 and Ra-224, respectively, in CaF_2-single crystals doped with Sm^{3+}.

Fig. 2 contains in addition some data on cation diffusion. The literature data [13] on self-diffusion of calcium (Ca-45) are represented by the full line. Some new results on the diffusion of Ra-224 in single crystals of CaF_2, BaF_2, and CaF_2/Sm^{3+} were obtained using the method of α-energy degradation [18] and are shown in fig. 2 as well. Cation diffusion is seen to proceed at a much lower rate than anion diffusion in both CaF_2 and BaF_2. Diffusion of Ra-224 in CaF_2 is slightly slower than diffusion of Ca-45. Adding Sm^{3+}-ions to CaF_2 yields an increase in Ra-224 diffusion rates (triangle in fig. 2 at $T = 970$°C). The two crystals of "pure" CaF_2 and of CaF_2/Sm^{3+} were annealed together to eliminate errors in temperature or annealing time.

5. Discussion

5.1. Fluorine Self-Diffusion

The present study provides tracer data on fluorine self-diffusion in single crystals of CaF_2 and BaF_2 in wide temperature ranges of 350 to 940°C for CaF_2 and 435 to 900°C for BaF_2. Intrinsic diffusion was observed in the whole temperature range for BaF_2 and above about 700°C for CaF_2. Excellent agreement is found with values calculated from the conductivity data of Barsis and Taylor [2], proving that the application of the Nernst-Einstein equation is justified. The data of Ure [1] are higher by about a factor of 3. The activation enthalpy, ΔH, for fluorine diffusion in CaF_2 is higher than that for BaF_2, as would be expected because of the higher melting point, T_m($\Delta H/T_m = 23.6$ cal/mole °K or 1.02×10^{-3} eV/°K for BaF_2 and 27.4 cal/mole °K or 1.19×10^{-3} eV/°K for CaF_2). The pre-exponential factors, D_0, are roughly of the order of magnitude expected for a volume diffusion process (3.1 and 50 $cm^2 sec^{-1}$).

The incorporation of trivalent fluorides such as SmF_3 into CaF_2 is thought to mainly lead to formation of anion interstitials as charge-compensating species, on the basis of experimental evidence of electron spin resonance, di-electric and anelastic relaxation, X-ray density, etc. (e.g. [19-21]). Therefore, the observed increase in fluorine diffusion should be due to the *extrinsic* mobility of fluorine interstitials, whereas both interstitials and vacancies contribute significantly to the intrinsic diffusion.

Since the fluorine vacancy and the fluorine interstitial have different mobilities, the Arrhenius plot in the intrinsic range should not be completely straight. However, no attempt was made to evaluate the data in this way, or to deduce the diffusion mechanism of the interstitial. In principle, transport mechanisms can be determined by comparing tracer diffusion coefficients (D_t and diffusion data, D_σ) computed from the ionic conductivity through the Nernst-Einstein relation. The correlation factor $f = D_t/D_\sigma$ is known for the three possible simple mechanisms of anion transport in the fluorite structure [22]: for (uncorrelated) interstitial diffusion, $f = 1$; for a vacancy mechanism, $f = 0{,}65$; for an interstitialcy mechanism, $f = 0.74$. Future work should determine the diffusion mechanism on this basis.

Below 700°C, a smaller ΔH was observed in CaF_2 owing to the onset of extrinsic diffusion. The knee temperature (and hence the pre-exponential term of the extrinsic process) depends on the effective impurity concentration. This explains the differences in the position of the knee in the present study and in those of Ure and of Barsis and Taylor. A constant ΔH of about 0.9 eV was obtained for the extrinsic diffusion, but no definite decision can be made whether this value should be attributed to the mobility of vacancies or of interstitials since the nature of the effective impurities is not known. The two most probable impurities would be alkali ions, e.g. Na^+, or else oxygen, O^{2-}. Introduction of oxygen in CaF_2 is known to enhance the low-temperature ionic conductivity [11, 23]. Fluorine vacancies are expected to dominate fluorine self-diffusion in such samples, and the activation enthalpies deduced (0.9 to 1.0 eV) match well the present value of 0.9 eV. Much lower values of the apparent activation enthalpy for anion vacancy motion have been obtained from e.g. nmr line-width measurements, for example $\Delta H_m = 0.36 \pm 0.06$ eV [12]. As pointed out by Rossing [24], an association between O^{2-} ions on anion sites and anion vacancies might explain this discrepancy. In this case, the activation enthalpy, Q, for anion diffusion would be [25]

$$Q = \Delta H_m + \Delta H_a/2.$$

Using $Q = 0.9$ eV and $\Delta H_m = 0.36$, the association energy ΔH_a would be 1.1 eV. Rossing [24] found $\Delta H_m = 0.56$ eV, $\Delta H_a = 0.52$ eV, which would yield a Q value of 0.82 eV which thus would be similar to the value observed here. Therefore, oxygen might be the relevant impurity for the observed extrinsic process for fluorine self-diffusion in CaF_2 below 700°C.

A rough value for the formation energy, ΔH_f, of anion Frenkel pairs can be deduced from the present results, neglecting entropy effects. ΔH_f would fall into the range $2 \times (2.0 - 0.9)$ eV to $2 \times (2.0 - 0.46)$ eV, with 0.46 eV being the average of the two above values of references 12 and 24. Hence, ΔH_f would be expected to fall into the range 2.2 to 3.1 eV.

If the effective concentration of impurities is estimated by comparing the D_0's for extrinsic and intrinsic diffusion, the experimentally observed knee temperature of about 700°C is obtained if a value of ≈ 2.3 eV is used to calculate the temperature where the thermally created defect concentration exceeds the impurity-controlled one. This is an additional argument in favour of the above range of values for the formation energy of anion Frenkel defects.

5.2. Cation Diffusion

The present data on cation diffusion confirm the previous statement [13] that the anion defects in CaF_2 and BaF_2 are much more mobile than the cation defects and that therefore the contribution of cations to the overall ionic conductivity is very small (roughly 10^{-7} to 10^{-6} between 900 and 1100°C; see fig. 4 of reference 13 for the dependence of the transference number of Ca in CaF_2 on temperature). The calculated energies of formation of defects (reference 9 and table I) suggest that a vacancy mechanism might govern cation diffusion, the vacancies probably being created as Schottky trios, i.e. stoichiometric, electrically neutral vacancy clusters consisting of one cation and two anion vacancies, since for both CaF_2 and BaF_2

$$\Delta G_S/3 \ll G_{FC}/2 \qquad (2)$$

ΔG_S and ΔG_{FC} = free energies of formation of Schottky trios, S, and cation Frenkel defects, FC, respectively.

TABLE 1 Summary of present and previous results on diffusion processes in CaF_2 and BaF_2

Material	BaF_2	CaF_2
Melting point, °K	1560	1687
ΔH for F-diffusion, eV	1.6 (p.s.)*	2.0 (p.s.)*
	1.64 [2]	2.13 [2]
D_0 for F-diffusion, $cm^2 sec^{-1}$	3.1 (p.s.)*	50 (p.s.)*
	6.2 [2]ᵃ	134 [2]ᵃ
Formation energy for anion Frenkel pair, eV	—	2.2-3.1 (p.s.)*
	1.58-1.78 [2]	2.8 [1]
	1.9 [4]	2.22-2.64 [2]
	†th 2.3 [9]	†th 2.7 [9]
Migration energy, eV, for anion interstitial	0.78 [2]	1.65 [1]
	0.79 [4]	—
	0.86 [10]	—
anion vacancy	0.85 [2]	0.52-0.88 [1]
	0.56 [3]	0.81-1.02 [2]
		0.9 [11]
		0.36 [12]
ΔH for cation diffusion, Ca	—	3.76 [13]
Sr	3.75 [14]	4.37 [14]
D_0 for cation diffusion, $cm^2 sec^{-1}$ Ca	—	130 [13]
Sr	4×10^3 [14]	2×10^5 [14]
Migration energy, eV for cation (estimated) Ca	—	1.5 ± 0.6 (p.s.)*
Formation energy, eV, for cation Frenkel pair, ΔG_{FC}	†th 8.8 [9]	†th 7.1 [9]
Schottky trio, ΔG_S	†th 5.2 [9]	†th 5.8 [9]

*p.s. = present study.
†th = theoretical values calculated by Franklin [9].
ᵃCalculated assuming the applicability of the Nernst-Einstein equation.

A simple thermodynamic treatment of the fluorite structure was previously performed for UO_2 and relevant experiments showed qualitative agreement [26-30]. The model essentially postulates a correlation between defects in the anion sublattice and the cation sublattice such that, if concentrations are defined *per site*, the concentrations of cation vacancies, N_{VC}, for the pure material and for a material doped with an impurity having a higher valence state than the cations of the lattice (e.g. Sm^{3+} in CaF_2), are given by the simplified expressions

$$CaF_2\,(N_{VC}) \approx 2\exp\{-(\Delta G_S - \Delta G_{FA})/kT\} \qquad (3a)$$

$$(Ca_{1-x}Sm_x)F_{2+x}\,(N_{VC}) \approx x^2\exp\{-(\Delta G_S - 2\Delta G_{FA})/kT\} \qquad (3b)$$

where FA stands for Frenkel defects in the anion sublattice. Therefore, additions of Sm^{3+}-ions to CaF_2 are expected to lead to an increase in N_{VC} and hence to an increase in cation diffusion rates, at least as long as the concentration of Sm^{3+} is $> N_{iA}$, the concentration of thermally created fluorine interstitials.

Such an effect has been observed (fig. 2) at 970°C with a total concentration of Sm of 0.24 mol %. For this temperature, the data of reference 1 yield $N_{iA} \approx 0.15\%$, which hence is smaller by a factor of about two than the concentration of Sm^{3+}. The observed increase in D_{Ca} by a factor of 4.4 is therefore of the order of the expected effect. Simultaneously, the observed increase in D_{Ca} indicates that Ca diffuses via a cation vacancy mechanism, since the above model would postulate a decrease in D_{Ca} in Sm^{3+}-doped CaF_2 for an interstitial mechanism for cation diffusion.

The observed ΔH for intrinsic cation diffusion consists, according to equation 3a, of three terms (neglecting entropy effects)

$$\Delta H \approx \Delta G_S - \Delta G_{FA} + \Delta H_m \qquad (4)$$

We can therefore obtain a rough estimate of the migration energy, ΔH_m, of the cation defect, which was assumed to be a cation vacancy, using the data of table I. We obtain $\Delta H_m \approx 1.5 \pm$

0.6 eV. Baker and Taylor [14] estimated a higher value of 2.1 ± 1.2 eV due to their higher ΔH for cation (Sr) diffusion in CaF_2, but their high ΔH was accompanied by a high D_0 (table I) which might point to a different diffusion mechanism (see below).

On the other hand, the present value of $\Delta H_m = 1.5 \pm 0.6$ eV compares favourably with the ΔH measured by Short and Roy [31] for extrinsic diffusion in polycrystalline CaF_2. The same authors observed, in agreement with the present result on $CaF_2 + SmF_3$, an increase of D_{Ca} in YF_3-doped CaF_2, as well as a decrease in NaF-doped CaF_2, thus again favouring a vacancy mechanism for cation diffusion.

Recent unpublished results of further studies [32,33]* of Ca-diffusion in CaF_2 tend to indicate a knee in the Arrhenius diagram at high temperatures near the melting point, i.e. above about 1100°C. At such temperatures in excess of 1100°C, a higher ΔH combined with a high value of D_0 are indicated. As pointed out by Baker and Taylor [14], such high ΔH's could either be due to excess impurity-induced anion vacancies and/or cation diffusion by means of associated vacancy pairs. In the former case, our model [27] postulates that ΔH increases by ΔG_{FA} and D_0 by N_{VA}^{-2}, whereas in the latter case ΔH would increase by $\Delta G_{FA} - \Delta H_a$, with ΔH_a = association energy for the pair formation, whereas D_0 would increase by $N_{VA}^{-1} \exp(-\Delta S_a/k)$.

6. Summary and Conclusions

The tracer diffusion data of the present study for fluorine self-diffusion in CaF_2 and BaF_2 are in agreement with previous ionic-conductivity studies, thus proving the applicability of the Nernst-Einstein relation. The intrinsic diffusion shows ΔH's of 1.6 eV for BaF_2 and 2.0 eV for CaF_2. The extrinsic behaviour of CaF_2 below about 700°C with a ΔH of 0.9 eV is probably due to incorporation of oxygen ions, O^{2-}. The formation energy of anion Frenkel defects is bracketed by the range 2.2 to 3.1 eV.

The fluorine defects, both vacancies and interstitials, are much more mobile than cation defects. Since, contrary to what is observed in materials showing a predominant Schottky disorder, doping with Sm^{3+} increases both anion and cation diffusion, the probable mechanism of calcium self-diffusion in CaF_2, at temperatures around 1000°C, is via a vacancy mechanism. The migration energy of this process was estimated to be about 1.5 ± 0.6 eV. A similar interrelation between anion and cation defects had previously been observed in the related substances with predominant anion Frenkel disorder, viz. UO_2 and UO_{2+x}. At temperatures near the melting point, vacancy pairs or Schottky-trios might contribute to calcium self-diffusion in CaF_2. Hence, cation diffusion processes in CaF_2 and BaF_2 are still far from being completely understood.

Future work should be concerned with the following open questions: For anion diffusion, the diffusion mechanism of the interstitial should be studied by comparing direct tracer diffusion data with diffusion data computed from ionic conductivity work. At temperatures near the melting point, a possible contribution of Schottky trios to fluorine mobility should be studied.

For cation diffusion, our present knowledge is not as complete as it is for anion diffusion, since the low mobilities of cations are more difficult to measure. Future work should be aimed at detecting and interpreting possible knees or curvatures in the Arrhenius diagram, to observe possible di- or tri-vacancy contributions to the diffusion mechanism, and to explain satisfactorily the high values of D_0.

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Note added in proof: M. F. Berard has recently (*J. Amer. Ceram. Soc.*) summarized his data on the diffusion of Ca in CaF_2. His diffusion coefficients are in fair agreement with those of reference [13] or of fig. 2 of the present study. In the temperature range 987 to 1246° C, Berard observes a ΔH of 4.15 ± 0.17 eV (96.0 ± 4 kcal/mole) and a D_0 of 5.35×10^3 cm^2 sec^{-1}. He explains this high value of D_0 on the basis of lattice strains introduced by formation and movement of mobile defects.

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