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CATION-DIFFUSION IN CaF_2 ABOVE AND BELOW THE TEMPERATURE OF THE λ-TRANSITION

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ABSTRACT

A λ-transition, evidenced by an anomaly in the specific heat, is known to occur in alkaline earth fluorides. In an attempt to learn more about the consequences of the connected dynamic disorder in the fluorine sublattice on the disorder in the metal sublattice, the diffusion of two cations, U and Pu, was studied above and below the transition temperature, T_λ in CaF_2 single crystals. U-diffusion was very slow and was best described by two lines in the Arrhenius diagram, thus indicating an interesting effect of the λ-transition on metal atom mobilities, metal atom defect concentrations, or cluster configurations. Pu diffusion was faster and no equally obvious effect of T_λ was observed. Some additional data are reported for Pu diffusion in $(Ba,U)F_{2+x}^{\lambda}$.

INTRODUCTION

A λ-transition, first reported in measurements of the specific heat, C_p of alkaline earth fluorides (ref.1), was also postulated for fluorite type oxides of technological interest (ref.2) since anion mobilities are similar in the two types of isostructural materials, if they are normalized to the melting point, T_m (in K). Fig. 1 illustrates the anomaly in C_p observed for fluorides and Table 1 summarizes the relevant results and predictions. Previously, the λ-transition was thought to be a cooperative process resembling somewhat that of fusion. Hence, the picture of anion-sublattice melting was used (or that of a transition from the normal fluorite structure MB_2 to a disordered structure where B-atoms are randomly distributed on both the tetrahedrally and the octahedrally coordinated sites). The increasing anharmonicity of fluorine (or oxygen) displacements with increasing temperature (ref.3) was thought to possibly be a precursor to these transitions.

Recent work by Schoonman (ref.4,5) on ionic conductivity in fluorides has prompted another picture. At a temperature, T_c, which is slightly higher than T_λ, a so-called Faraday transition, evidenced by a negative deviation from the Arrhenius relation in ionic conductivity, occurs. At T_c, anion vacancies $V_F^{\cdot}$ in

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the fluorides have a large and constant mobility μ

$$\mu(V_F^{\cdot}) = (2.6 \pm 0.3) \times 10^{-3}\ cm^2V^{-1}s^{-1} \qquad (1)$$

Schoonman suggests that at T_c only small concentrations of defects are present, typically 0.5 - 2 mol.%, which, however, show an unusually large defect mobility at T_c. Both halide ion vacancies and interstitials contribute to the conductivity. The mechanism for the high mobility with a low activation enthalpy involves the displaced ions around the Willis-type (ref.6) or similar clusters (non-collinear intersticialcy mechanism). In consequence, a small fraction of very mobile anti-Frenkel defects is suggested to cause conductivity values typical for molten salts.

TABLE 1: Properties of fluorite type materials of interest for a possible Lambda-transition

Substance	T_m,K	T_λ,K [a]	T_λ/T_m	ref.	log D cm^2s^{-1} at T_λ	log $\sigma(F_i)$ $\Omega^{-1}cm^{-1}$ at T_λ	ref.
fluorides							
CaF_2	1687	1430	0.85	1	- 5.5	- 0.1	7,5
SrF_2	1730	1400	0.81	8	-	- 1.1	-,5
BaF_2	1560	1230	0.79	8	- 6.0	- 1.0	7,5
ß-PbF_2	1095	(≳705)	(≳0.64)	5,9	-	- 0.9	-,5
others							
$SrCl_2$	1145	970	0.85	1	-	-	- -
K_2S	1220	1050	0.86	1	-	-	- -
oxides		predicted [b]			c)		
UO_2	3150	2680	-	-	-4.8(-3.3)	-	10,-
ThO_2	3570	3030	-	-	- 4.7		10,-
PuO_2	~2720	~2310	-	-	- 6.0	-	10,-
CeO_2	~2870	~2440	-	-	- 5.8	- 1	11,11
ZrO_2	~3000	~2550	-	-	(- 4)	-	10,-

a) No distinction is made between T_λ, the temperature of the specific heat anomaly, and T_c, the temperature of the Faraday-transition (negative deviation from the Arrhenius relation in conductivity)

b) assuming $T_\lambda/T_m = 0.85$

c) Chemical diffusion coefficients $\tilde{D}$, for $MO_{2\pm x}$, in brackets. Note that all these oxides are non-stoichiometric and that D and σ depend on oxygen partial pressure.

Note that reported values of T_λ and T_c show scatter, probably due to the reactivity of the fluorides towards traces of O_2 and H_2O. For example, literature values for T_c in PbF_2 vary between 725 and 780 K.

The nuclear fluorite type oxides exhibit diffusion properties that resemble closely those of the fluorides when corrected for the higher melting points (ref.10). The oxygen atoms also show anharmonic vibrations similar to those of the fluorine atoms in fluorides.

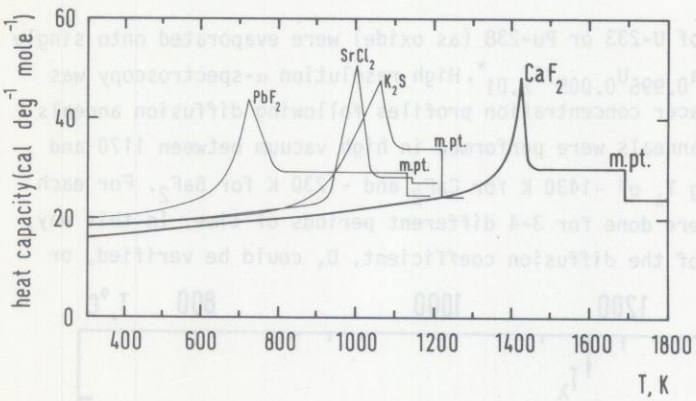

Fig. 1
The heat capacity, C_p, of substances with the fluorite structure showing an anomaly at about 0.85 T_m (refs.1,5,9)

A possibility to learn more about the high temperature disorder in the fluorite structure is to perform diffusion measurements. Measurements of fluorine self-diffusion in CaF_2 and BaF_2 were unfortunately not extended to the lambda-transition temperature (ref.7). The most interesting point would be to learn more about the possible consequences of the dynamic disorder in the anion sublattice above about 0.8 T_m on the disorder in the metal sublattice. The metal atoms are the slow species in the fluorite structure. Their mobility determines therefore interesting diffusion controlled mass transport processes (e.g. grain growth, creep, sintering etc.). If one chooses the picture of isolated randomly distributed anion defects then, as shown in (refs.10,12), via the Frenkel defect equilibrium between anion defects and the Schottky equilibrium (constant K_S) between anion vacancies, V_A, and cation vacancies, V_M, there should be a corresponding change in defect concentration and/or vibrational properties and/or cluster configurations in the metal sublattice. Thus

$$D_M \propto [V_M] \text{ and } [V_M] \cdot [V_A]^2 = K_S \qquad (2)$$

This question has also a technological relevance: Diffusion of the fission rare gases Kr and Xe that are formed in nuclear fuels in great concentrations and that can cause the fuel to swell, is intimately related to cation diffusion and may thus at high temperatures be affected in a so far unknown way. None of the nuclear fuel performance codes, so far, allows for this transition. An attempt to perform uranium self-diffusion measurements with UO_2 above the predicted lambda-transition temperature (Table 1) has failed so far due to pronounced evaporation effects masking diffusion. Therefore, another experimental approach was adopted and the diffusion of U and Pu was measured in CaF_2 where

a λ-transition is known to occur. CaF_2 is isostructural with UO_2, ThO_2 and PuO_2 and was previously and successfully used as model substance for measurements of diffusion properties in these actinide dioxides (ref.13).

RESULTS AND DISCUSSION

Thin tracer layers of U-233 or Pu-238 (as oxide) were evaporated onto single crystals of CaF_2 or $(Ba_{0.995}U_{0.005})F_{2.01}$*. High resolution α-spectroscopy was used to measure the tracer concentration profiles following diffusion anneals (e.g.refs.10,12). The anneals were performed in high vacuum between 1170 and 1550 K, thus bracketing T_λ of ~1430 K for CaF_2 and ~1230 K for BaF_2. For each temperature, anneals were done for 3-4 different periods of time. In this way, the time-independence of the diffusion coefficient, D, could be verified, or

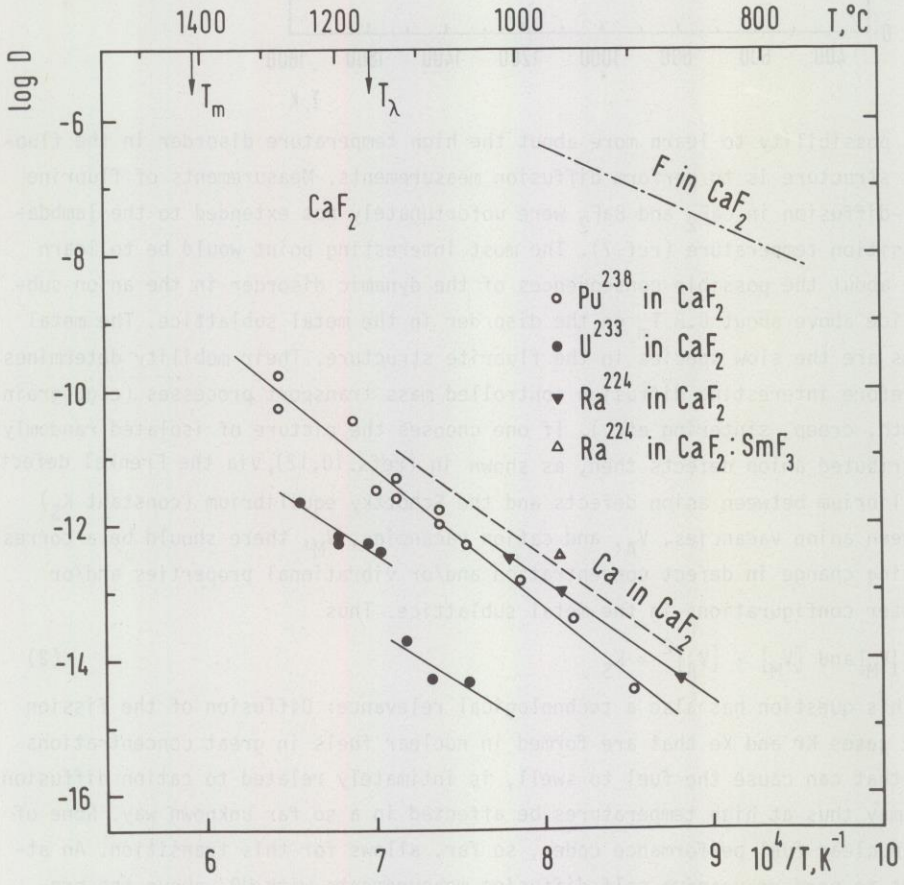

Fig.2. Arrhenius diagram of the diffusion of U^{233} and Pu^{238} in CaF_2 single crystals. Results for F^{18}, Ca^{45} and Ra^{244} are included for comparison (refs.7,13,14).

* These crystals were kindly provided by Dr. J. Schoonman, State University, Utrecht, The Netherlands

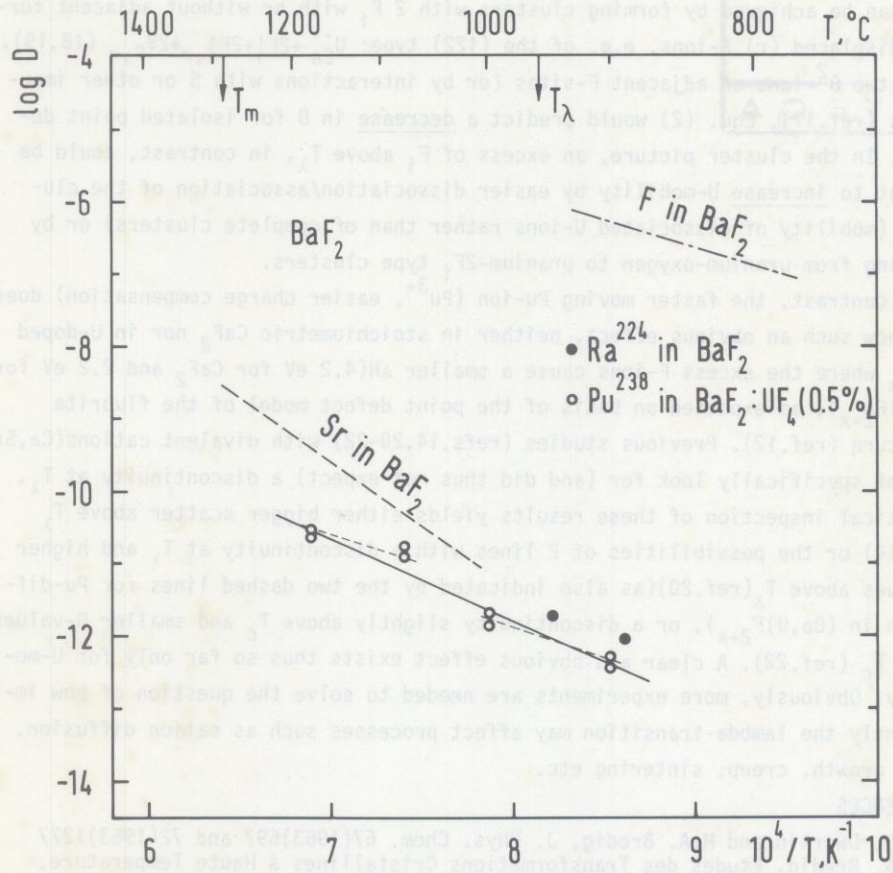

Fig. 3. Arrhenius diagram of the diffusion of Pu^{238} in $(Ba_{0.995}U_{0.005})F_{2.01}$. For comparison, results for the diffusion of F^{18}, Ra^{224} and Sr (deduced from chemical diffusion) in pure BaF_2 are shown (refs.7,15).

disturbing phenomena (evaporation-condensation processes, temporary precipitation of part of the tracer as an oxide on the surface of the specimens or surface relaxation effects (e.g. ref.12) etc.) could be corrected for since their time dependence is different from that of bulk diffusion which follows at $t^{1/2}$-law. The results obtained in this way are shown in Figs. 2. and 3.

The slowest moving cation is U which may be assumed (refs.16,17) to be present as U^{4+} (in contrast to Pu which probably is largely Pu^{3+}, and Ra, Sr and Ca which are divalent). It seems meaningless to describe the data for U with one Arrhenius type line since this would give a poor fit, a very high pre-exponential factor, D_o, of~10^{10} cm^2s^{-1} and a very high activation enthalpy, ΔH, of ~6.7 eV. The data are better described by two lines (see Fig. 2) with a discontinuity at T_λ and ΔH's of 3.1 and 3.2 eV above and below T_λ. The discontinuity corresponds to a sudden change in D by a factor of 10. It indicates thus an essential effect of the λ-transition on uranium atom mobilities. Charge compensation for U^{4+} in

CaF_2 can be achieved by forming clusters with 2 F_i with or without adjacent further displaced (r) F-ions, e.g. of the (122) type: $U^{\bullet\bullet}_{Ca}+2F'_i+2F'_{i,r}+2V^{\bullet}_{F,r}$ (18,19), or by two O^{2-}-ions on adjacent F-sites (or by interactions with S or other impurities (ref.17)). Equ. (2) would predict a decrease in D for isolated point defects. In the cluster picture, an excess of F_i above T_λ, in contrast, could be thought to increase U-mobility by easier dissociation/association of the clusters (mobility of dissociated U-ions rather than of complete clusters) or by changing from uranium-oxygen to uranium-$2F_i$ type clusters.

In contrast, the faster moving Pu-ion (Pu^{3+}, easier charge compensation) does not show such an obvious effect, neither in stoichiometric CaF_2 nor in U-doped BaF_{2+x} where the excess F-ions cause a smaller ΔH(4.2 eV for CaF_2 and 2.2 eV for $(Ba,U)F_{2+x}$), as expected on basis of the point defect model of the fluorite structure (ref.12). Previous studies (refs.14,20-22) with divalent cations(Ca,Sr) did not specifically look for (and did thus not expect) a discontinuity at T_λ. A critical inspection of these results yields either bigger scatter above T_λ (ref.14) or the possibilities of 2 lines with a discontinuity at T_λ and higher D-values above T_λ(ref.20)(as also indicated by the two dashed lines for Pu-diffusion in $(Ba,U)F_{2+x}$), or a discontinuity slightly above T_c and smaller D-values above T_c (ref.22). A clear and obvious effect exists thus so far only for U-mobility. Obviously, more experiments are needed to solve the question of how importantly the lambda-transition may affect processes such as cation diffusion, grain growth, creep, sintering etc.

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