Dipole Reorientation Kinetics in Rare Earth-Doped CaF$_2$

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The thermal depolarization technique has been used to determine the kinetics of defect dipole reorientation in single crystal CaF$_2$ doped with 0.01 mol% Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Yb and 0.05mol% Er. The activation energy for dipolar reorientation W was found to be 0.53 ± 0.05 eV over the entire lanthanide series. Least-mean-square analysis of the average values of relaxation time τ_0 at $1/T = O(K^{-1})$, showed a variation from 6×10^{-17} sec for Ce-doped samples to 4×10^{-18} for those containing Yb, the estimated error of any one measurement being $10^{\pm 1.5}$ sec.

The magnitudes of the observed values of W and τ_0 are supported by an analysis of the energetically most probable dipole reorientation mechanism, interstitialcy migration. The vibrational frequencies to be expected for interstitial ions and the entropy of activation are also discussed in terms of the experimentally observed kinetic parameters.

Introduction

Investigations of the kinetics of motion of the fluorine interstitial ion, F$_i'$, in CaF$_2$ doped with trivalent cationic solutes have been reported a number of times in recent years (1–13). The values reported for the energy of motion W and the relaxation time τ_0 at $1/T = O(K^{-1})$ measured using a variety of experimental techniques and solute ions are compiled in Table I. These results have been obtained from different samples with a variety of histories over a period of about 14 years, and it is readily apparent that gross discrepancies exist in the reported values.

This paper describes a number of experiments performed upon a set of single crystal CaF$_2$ samples containing the entire series of lanthanide rare earths as solutes. The kinetic parameters related to the reorientation of solute–interstitial dipoles were measured by use of the very sensitive thermal depolarization method, thus giving information about the motion of fluorine interstitials in the vicinity of these aliovalent solutes.

Theory

The thermal depolarization (TDP) method was first described by Bucci and Fieschi (14)

who called it the "ionic thermocurrent" (ITC) technique because of its similarity to the phenomenon of thermoluminescence. We prefer to use the term "thermal depolarization," as it is more descriptive of the actual process involved. A general description of the technique was included in the original paper and also in that of Bucci et al. (15).

The thermal depolarization technique consists of two essential steps: (i) The normally random dipole orientation distribution is perturbed so that the sample becomes macroscopically polarized in the direction of an applied field. (ii) Upon the influence of thermal energy, the dipolar orientation distribution again becomes random; and in doing so, a current is caused to pass through an external electrical circuit. This second step is normally accomplished by continuous heating of the sample at a constant rate. The expression describing the resulting thermal depolarization current is,

$$i(T) = \frac{\alpha N_d E p^2}{k T_p} [1 - \exp(-t_p/\tau(T_p))]$$
$$\times [\tau_0^{-1} \exp(-W/kT)]$$
$$\exp\left[\int_0^T -(b\tau_0)^{-1} \exp(-W/kT)dT\right], \quad (1)$$

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TABLE I

Activation Energy for Motion W and the Relaxation Time τ_0 at $1/T = O(K^{-1})$ of Fluorine Interstitials in CaF_2 Containing Some Trivalent Cationic Solutes

Solute	Technique	Temp. (K)	W (eV)	τ_0 (sec)	Ref.
Y	Elec. cond.	963–1193	1.65 ± 0.35		(1)
	Elec. cond.	873–1573	1.56		(2)
Dy	Optical	873–1223	1.5		(3)
Y	Elec. cond.	373–1173	1.02		(4)
	Diel. loss	373–673	1.16 ± 0.08	3×10^{-14}	(5)
Sm	Diel. loss	373–773	1.4		(6)
	NMR	77–1300	0.53 to 2.4		(7)
	NMR	400–700	0.63	6.7×10^{-14}	(8)
Gd	ESR/diel. loss	350–450 200–260	0.38	8.2×10^{-14}	(9)
	TDP	140	0.39 ± 0.01	$1.2 \pm .7 \times 10^{-13}$	(10)
	TDP	60.5	0.167 ± 0.005	$2 \pm 1 \times 10^{-13}$	(10)
Er	TDP	138	0.386 ± 0.008	$2 \pm 0.3 \times 10^{-13}$	(10)
	TDP	54	0.147 ± 0.004	$3 \pm 2 \times 10^{-13}$	(10)
Ce	TDP	147	0.46 ± 0.02	$6 \pm 4 \times 10^{-15}$	(11)
Er	ESR	473	1.0 ± 0.1	$10^{-13 \pm 2}$	(12)
Y	Anelastic loss	600	1.2	10^{-15}	(13)

where

α geometrical factor dependent upon the crystal structure

N_d total dipole concentration

E electric field

p dipole moment

k Boltzmann's constant

T_p polarization temperature (K)

t_p polarization time

$\tau(T_p)$ dipole relaxation time at T_p

τ_0 dipole relaxation time at $1/T = O(K^{-1})$

T instantaneous temperature (K)

W activation energy for dipolar reorientation

A detailed analysis of the derivation of this expression in terms of the polarization and depolarization process will not be presented here, but can be found elsewhere (16).

The low temperature portion of the $i(T)$ curve, which rises to a peak and then falls off again as the temperature is raised, may be expressed as

$$i(T) = P_0 \tau_0^{-1} \exp(-W/kT), \qquad (2)$$

where P_0 is the total initially induced polarization. This expression is valid only well below the peak maximum, where a truly linear relation between $\log i$ and $1/T$ can be experimentally verified. It can be easily shown that the area under the $i(T)$ curve is proportional to the value of P_0.

The following expression for the relaxation time at any temperature can also be derived from Eq. (1):

$$\ln \tau = \ln \tau_0 + W/kT = \ln \int_{i(T)}^{\infty} i(t)dt - \ln i(T). \quad (3)$$

It will be noted that this expression does not require a linear relationship between time and temperature during the experiment. Equation (3) was used throughout this work to derive values of W and τ_0.

Experimental Procedure

The primary series of samples of rare earth-doped CaF_2 were supplied by F. K. Fong of Purdue University. An additional Gd-doped sample was obtained from A. D. Franklin of the National Bureau of Standards for comparison

TABLE II

DETAILS OF INDIVIDUAL SAMPLES OF RARE EARTH-DOPED
CaF_2

Solute	Dopant conc (mole %)	Contact area (cm^2)	Thickness (cm)
Ce	0.01	0.709	0.145
Pr	0.01	0.704	0.137
Nd	0.01	0.704	0.137
Sm	0.01	0.709	0.137
Eu	0.01	0.709	0.132
Gd	0.01	0.724	0.140
Tb	0.01	0.709	0.140
Dy	0.01	0.716	0.140
Ho	0.01	0.721	0.130
Er	0.05	0.711	0.137
Tm	0.01	0.716	0.137
Yb	0.01	0.716	0.140
Gd[a]	0.01	0.112	0.104

[a] Sample provided by A. D. Franklin; the others were from F. K. Fong.

purposes. Details concerning the individual samples are given in Table II. It should be noted that the solute concentrations cited for the samples from F. K. Fong are the concentrations in the melt before the crystals were grown, and may be somewhat higher than that actually present in the resultant crystals. The concentration given for the sample from A. D. Franklin was determined by analysis.

All samples were single crystals without any evidence of precipitation, with (111) faces in the plane of the contacts. Colloidal graphite was used as the electrode material.

Figure 1 shows the basic configuration of the sample holder and its more important dimensions. The lower contact is silver-plated copper and can be rapidly cooled by the direct introduction of liquid nitrogen into the central cavity. The temperature is monitored by means of a copper/constantan thermocouple imbedded in the top
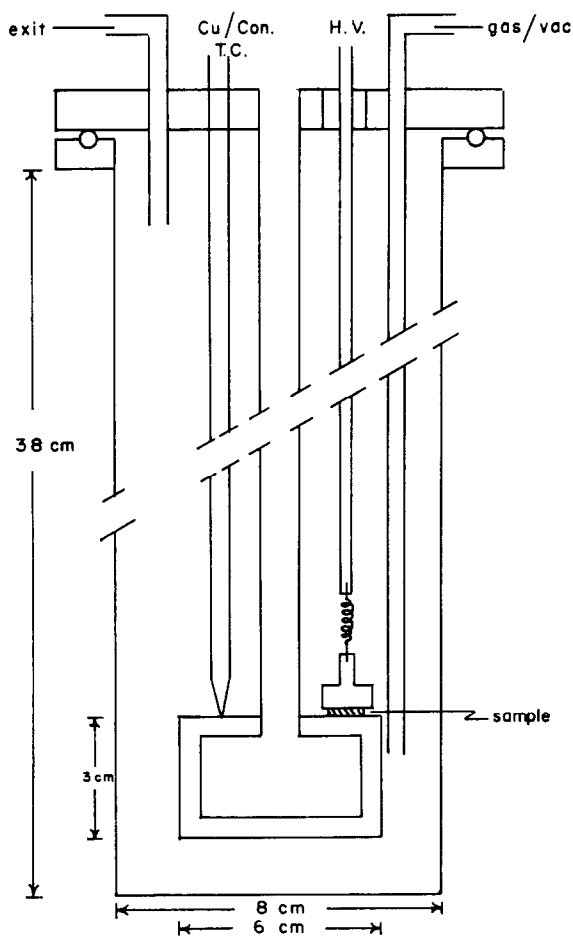

FIG. 1. Schematic diagram of sample holder.

surface of the lower contact. Due to the low values of current which must be measured, it is impossible to monitor the temperature of both sides of the sample simultaneously. Provision was made for evacuating the sample chamber with a vaccum pump and also for providing an inert atmosphere such as nitrogen or helium.

The upper contact is also silver-plated copper and is attached to a thin-walled (0.010 in.) stainless steel tube by means of a small stainless steel spring to maintain good contact. This top contact is the "high" lead of the system and the lower contact is grounded. The ground contact is common to all parts of the equipment and also to a copper mesh screen, which completely surrounds the entire apparatus. The central tube supporting the lower contact and through which the liquid nitrogen passes is also thin-walled stainless steel to reduce thermal losses.

Careful control of the liquid nitrogen level in an external Dewar surrounding the whole sample chamber allows the production of a relatively constant sample temperature over a wide range for use in the polarization portion of the experiment.

After polarization and quenching, the heating rate can be varied by introducing hot nitrogen gas at a controlled rate into the central cavity by passing it through a small gas heater. If desired, the rate may also be changed by use of an external electrical heater. It was found, however, that a good linear heating rate could be achieved over the range of the TDP peaks investigated in this study by simply allowing the system to rise to room temperature by complete removal of the external Dewar.

The depolarization current measurements were made by use of a Carey Model 401 vibrating reed electrometer with a reported noise level of 5×10^{-17} A. The output of this electrometer was fed to two recorders simultaneously, a large chart recorder with a chart speed of 2 in./min from which individual current measurements could be taken as a function of time, and a smaller recorder with a very much slower speed chart, which provided a more compressed, but comprehensive record of all portions of each run. The thermocouple output was recorded concurrently with the current measurements on another recorder. The polarizing potential was applied by means of the top contact, using a stabilized dc power supply with a maximum of 500 V.

Two sets of experiments were performed; the first at a polarizing field strength of 1500 V/cm

and polarization temperatures near room temperature to insure that all possible peaks would be observed. A second group of experiments used a polarization field of 3000 V/cm and T_p values slightly above the temperatures of the peak maximums observed in the initial experiments. In order to improve the signal-to-noise ratio and allow more sensitive scale factors to be used, this set of experiments used a longer instrumental time constant, necessitating corrections during the data analysis.

All the samples, except the one containing thulium, showed the existence of a single major peak at about 150K, uncomplicated by any apparent overlapping peaks. The thulium-containing sample did show a second peak (at 168K) and also a distinctly misshapen high temperature tail on the major peak. Since this sample was seemingly atypical and probably contaminated, the results obtained from it are not included in the compilation of experimental data presented later.

Experimental Results

A typical example of the observed variation of the thermal depolarization current with temperature is shown in Fig. 2. The corresponding $\log i$ versus $1/T$ and $\log \tau$ versus $1/T$ curves are shown in Figs. 3 and 4, respectively. The data points shown on these figures were calculated and plotted using computer techniques. The activation energy for dipolar reorientation W was obtained from a least-square fit of the slope of the linear portion of Fig. 4, and τ_0 by the intercept at $1/T = O(\text{K}^{-1})$ in accordance with Eq. (3).

The values of W obtained from the two sets of measurements are shown in Fig. 5 as a function of the atomic number of the solute ion. The bars indicate the estimated errors between the two groups of measurements, ± 0.05 eV, and the solid line is the least-square fit to the data points. Figure 6 indicates the variation of τ_0 with the atomic number of the solute ion. The estimated error, $10^{\pm 1.5}$, in τ_0 was calculated from the estimated error in W. The dotted line is the least-square fit to the data points. These data are also presented in Table III. As shown, the experimentally determined values from the Gd-doped sample of CaF_2 supplied by A. D. Franklin were in excellent agreement with the results obtained from the other Gd-doped sample.

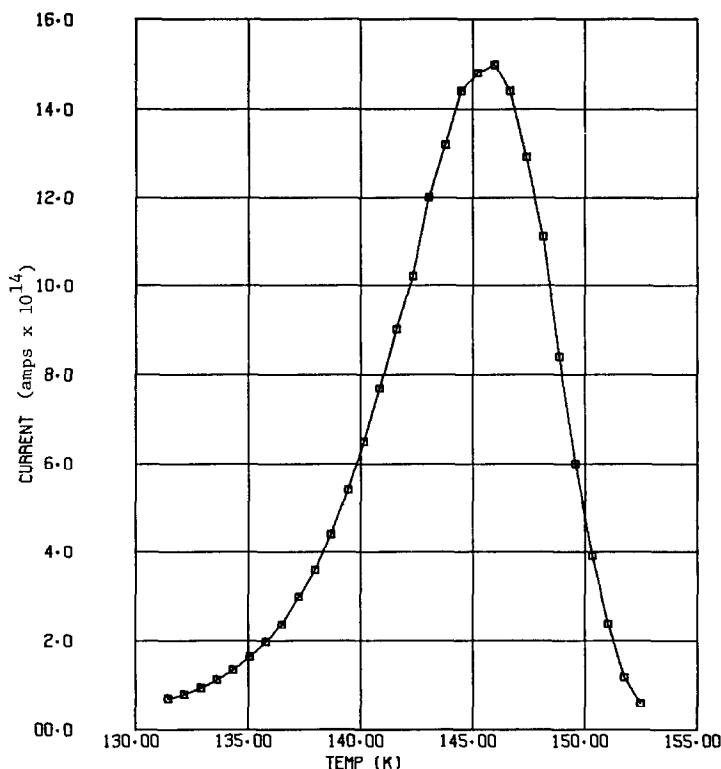The dipole concentrations N_d calculated from the experimentally determined values of induced

FIG. 2. Thermal depolarization current as a function of temperature for Er-doped CaF_2 sample: $E_p = 1500$ V/cm at 252K.

polarization, assuming a hard sphere model of the CaF_2 structure with a dipole moment of 4.37×10^{-27} cm–C are also included in Table III. These values of dipole concentration were experimentally reproducible within a factor of two for any given sample.

Discussion

Relation Between These Results and Previous Work

It is difficult to obtain precise values of the activation energy from a relatively few measurements over a narrow temperature range. As a result, one often finds discrepancies between activation energy data reported by different investigators, even though the absolute magnitudes of the observed relaxation times are quite similar. Furthermore, since relaxation phenomena are generally described by an expression of the form

$$\tau = \tau_0 \exp(W/kT), \qquad (4)$$

the sensitivity of the exponential term to variations in the value of W may produce wide variations in the values of τ_0 derived from different experiments. If relaxation time information relating to the same physical phenomenon is obtained over a wide temperature range by the use of several experimental methods, a good indication of the consistency between the various collections of data is obtained by plotting the observed relaxation times as a function of temperature, using appropriate coordinates. An outstanding example of this is the motion of interstitial carbon in iron. In this case, it has been shown (17) that a simple Arrhenius relation of the form of Eq. (4) is obeyed over 14 orders of magnitude in the diffusion coefficient.

The correlation between the results obtained in this study with several other related investigations is illustrated in Fig. 7. Included on this semilog plot are the τ data on Gd-doped CaF_2 reported by Franklin and Marzullo (9) by use of the ESR and dielectric loss methods, the TDP results of Stott and Crawford (10), and the values of τ found in this work for similar samples at both 1500 and 3000 V/cm. The broken line is an extrapolation of the present data. Note that Fig. 7

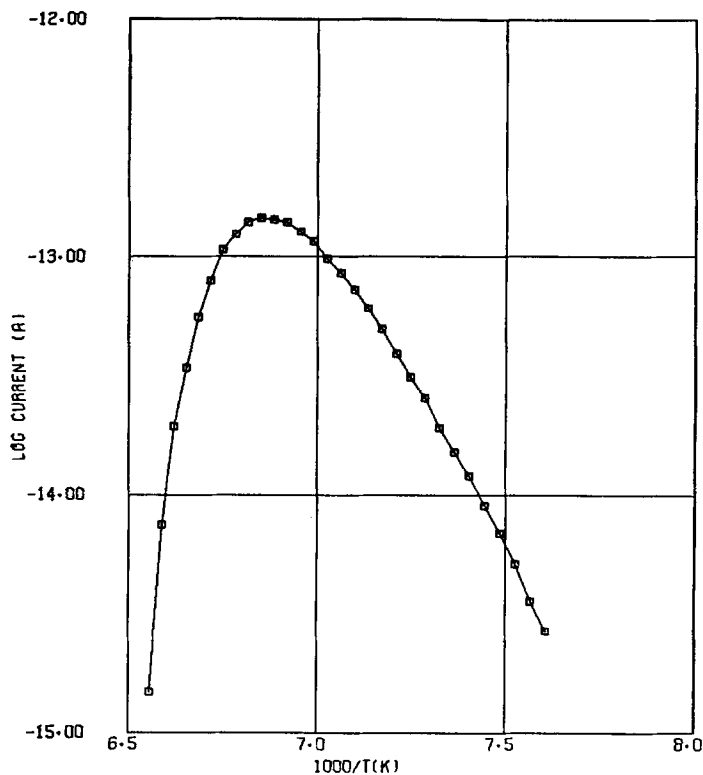STIEFBOLD AND HUGGINS

FIG. 3. Log i versus $1000/T$ curve for Er-doped CaF_2 sample: $E_p = 1500$ V/cm at 252K.

covers a range of almost 6 in reciprocal temperature and more than 12 orders of magnitude in τ. Values extrapolated from this work are less than one order of magnitude different from either set of Franklin and Marzullo's data. Some preliminary dielectric loss measurements made in this laboratory (18) on the samples used for these TDP experiments are also included in Fig. 7.

The Activation Energy for Dipolar Reorientation

The data compiled in Table III and Fig. 5 indicate that the activation energy associated with dipolar reorientation in CaF_2 doped with the whole series of trivalent lanthanide elements is 0.53 ± 0.05 eV. There is no apparent variation with the atomic number of the solute, as a least-square fit of the points in Fig. 5 resulted in a slope of only 6×10^{-4} eV/atomic number unit, which is well within the experimental precision. This value of activation energy compares favourably with the value reported for a thermal depolarization experiment performed on a Ce-doped sample by Royce and Mascarenhas (11), who also used the TDP technique. Excellent agreement is also seen with the activation energy for motion,

obtained at low temperatures, for samples containing Sm found by Lysiak and Mahendroo (7) using NMR techniques, and 0.1 eV below the NMR value reported by Viegle (8). However, the activation energy values reported here are all well above the value of 0.39 eV obtained by Stott and Crawford, who also used the TDP technique (10), on a sample of Gd-doped CaF_2. These latter authors have also reported (10) an activation energy of 0.39 eV on Er-doped sample. Franklin and Marzullo (9) gave values of $W = 0.40$ and 0.39 eV for ESR and dielectric loss experiments, respectively, on Gd-doped samples containing 0.08 mol% GdF_3.

The discrepancy between the results reported here on Gd- and Er-doped CaF_2 and those reported by Stott and Crawford using the same technique could certainly, in some part, be related to difference in the samples and their history. On the other hand, the handling of the data in the two laboratories was also decidedly different. The values of the activation energy for motion in this work were derived by use of the entire experimental curve through the use of Eq. (3). This was also the technique selected by Royce
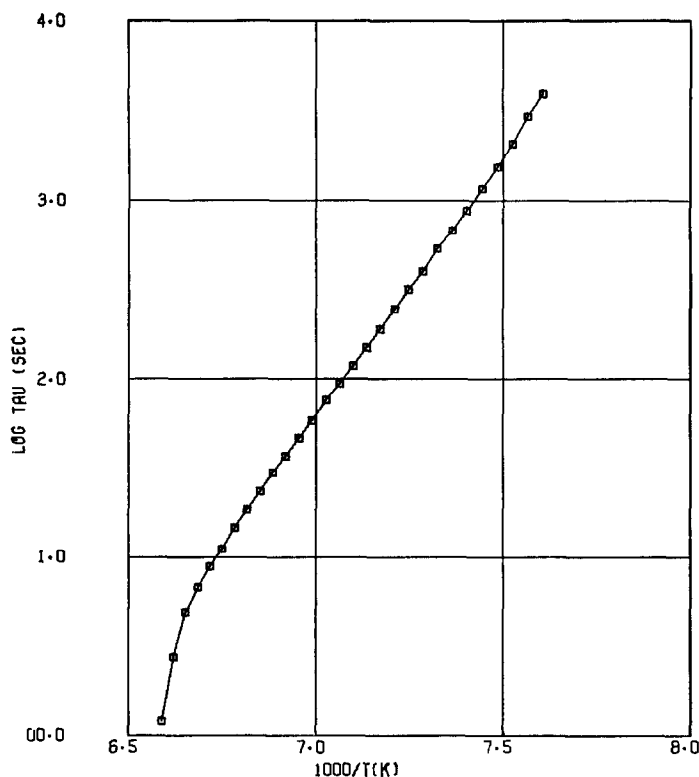
FIG. 4. $\log \tau$ versus $1000/T$ curve for Er-doped CaF_2 sample; $E_p = 1500$ V/cm at 252K.

and Mascarenhas (*11*) in their work on Ce-doped CaF_2. On the other hand, Stott and Crawford (*10*) used a curve-fitting technique.

The disparity between results obtained in different laboratories upon different samples may also be due to a dependence of the activation energy and τ_0 upon the concentration of solute. This has been observed in Ce-doped samples containing 0.10 mol% solute (*11*). The present authors have also observed similar changes in both W and τ_0 in a series of Gd-doped CaF_2 samples (*19*).

In experiments in which long-range motion of isolated fluorine interstitials is measured, such as the electrical conductivity measurements cited in Table I, as well as the optical experiments of Fong and Hiller (*3*), one may expect the experimentally derived energy for motion to be different than that obtained for local reorientation of bound dipoles, as measured by the TDP technique. The origin of this difference is associated with the nature of the distortion in the region of the $(RE_{Ca}^\circ : F_i')$ dipole. ENDOR measurements (*20*) have shown that in the nearest-neighbor dipole configuration the RE_{Ca}° is moved off center

from the normal cation site by 6% in the direction of the F_i'. The eight anions neighboring the F_i' are also displaced radially outward by 9%. This distortion, giving rise to the observed tetragonal symmetry in the region of the dipole, would be expected to reduce the energy required for local interstitial motion, and thus dipole reorientation, below that required for movement of an isolated F_i' from one equivalent site of cubic symmetry to another.

It is also true that electrical conductivity measurements sense the integrated contribution of all charged species and can, therefore, be difficult to interpret unambiguously. This argument has recently been reinforced by Chen (*21*), and is particularly relevant to measurements made at higher temperatures. It is known, for example, that oxygen dissolves readily in CaF_2 at relatively low temperatures and its presence has been detected in CaF_2 by optical absorption and ESR spectrum analysis (*22*). In CaF_2 samples deliberately doped with low concentrations of trivalent solutes, the additional presence of oxygen ions will compensate an equivalent amount of charge. This will have the effect of
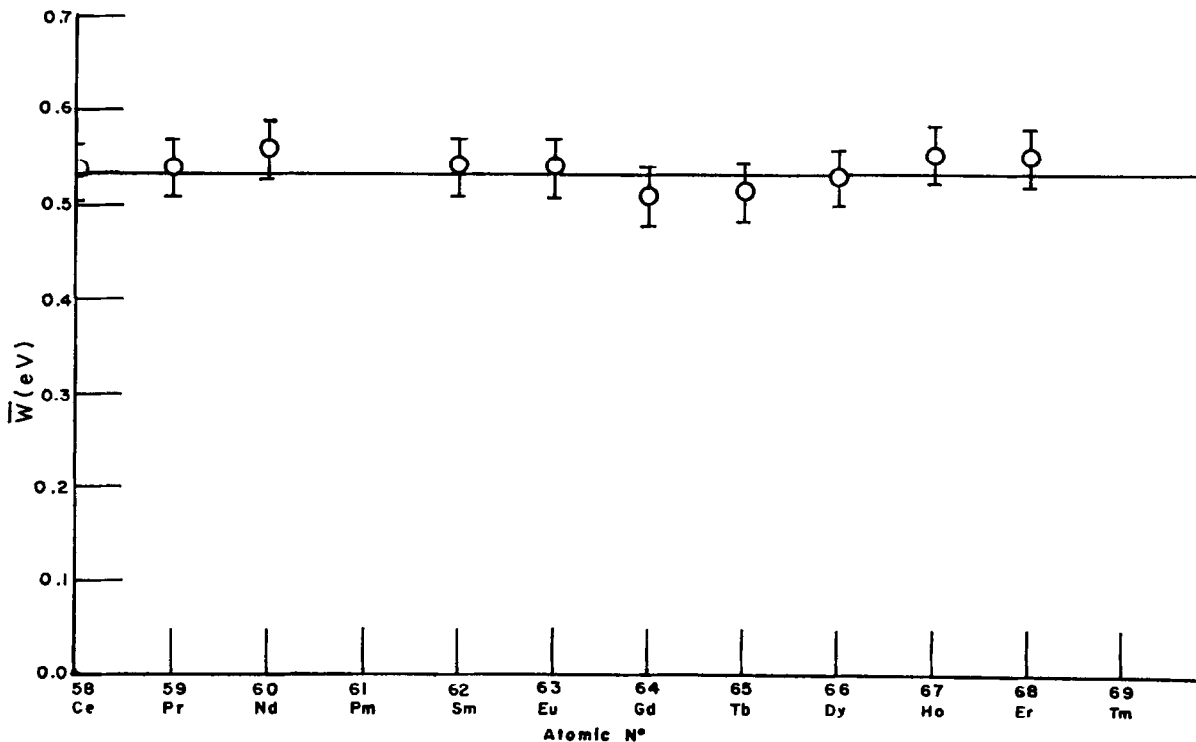
FIG. 5. Values of activation energy for interstitial motion as a function of atomic number of solute ions.

reducing the expected number of F_i' ions. If the oxygen ion concentration is greater than the trivalent ion concentration, the sample will conduct via the V_F° mechanism, rather than by interstitial migration. Since the O^{2-} ions can be expected to associate, at least in part, with the trivalent solute ions, this additional lattice strain which is recognized by ESR methods as a site with trigonal symmetry (22) can also be expected to influence the motion of nearby F_i' ions.

Dielectric and anelastic loss measurements are expected to yield comparable results to those obtained by the TDP method on samples containing defect dipoles. However, as Barsis and Taylor (23) have recently pointed out, there are still significant problems of interpretation, primarily with respect to the rationalization of the magnitude of the peaks observed with the known impurity content for postulated loss mechanisms. Franklin and Marzullo (9) suggested that the comparatively high values of W reported by Chen and McDonough (5, 6) for the energy for motion of the F_i' could be due to a highly conducting surface layer related to oxygen contamination.

The ESR experiments of Twidell (12) seem to give an energy for motion of fluorine interstitials which is anomalously high. It should be noted, however, that he proposed that the F_i' motion in that case was from a next-nearest-neighbor (nnn), to a nearest-neighbor (nn) position (relative to Er_{Ca}°). This is a different type of jump from that considered in this work.

The low temperature TDP peaks observed by Stott and Crawford (10) with activation energies of about 0.15 eV were tentatively assigned by them to a (nnn)→(nnn) transition of the F_i' with respect to the RE_{Ca}° ion. They were not observed in the experiments reported here, as they are found below 78 K.

The published values of the activation energy for V_F° motion are generally very close to the value 0.53 ± 0.05 eV found in this work, for the energy for motion of F_i'. This is not an unexpected result, as similar observations have been made in other alkaline earth halides with the same structure. In SrF_2, Bollmann et al. (4) reported that the energies for motion of both V_F° and F_i' are 0.94 eV. Similarly, Barsis and Taylor (24) found $W(V_F^\circ) = 0.78$ eV and $W(F_i')$ = 0.85 eV in BaF_2. The acceptance of the assumption that the interstitialcy mechanism is operative in this system (4, 25) argues in favor of this comparability in activation energy values. Be-
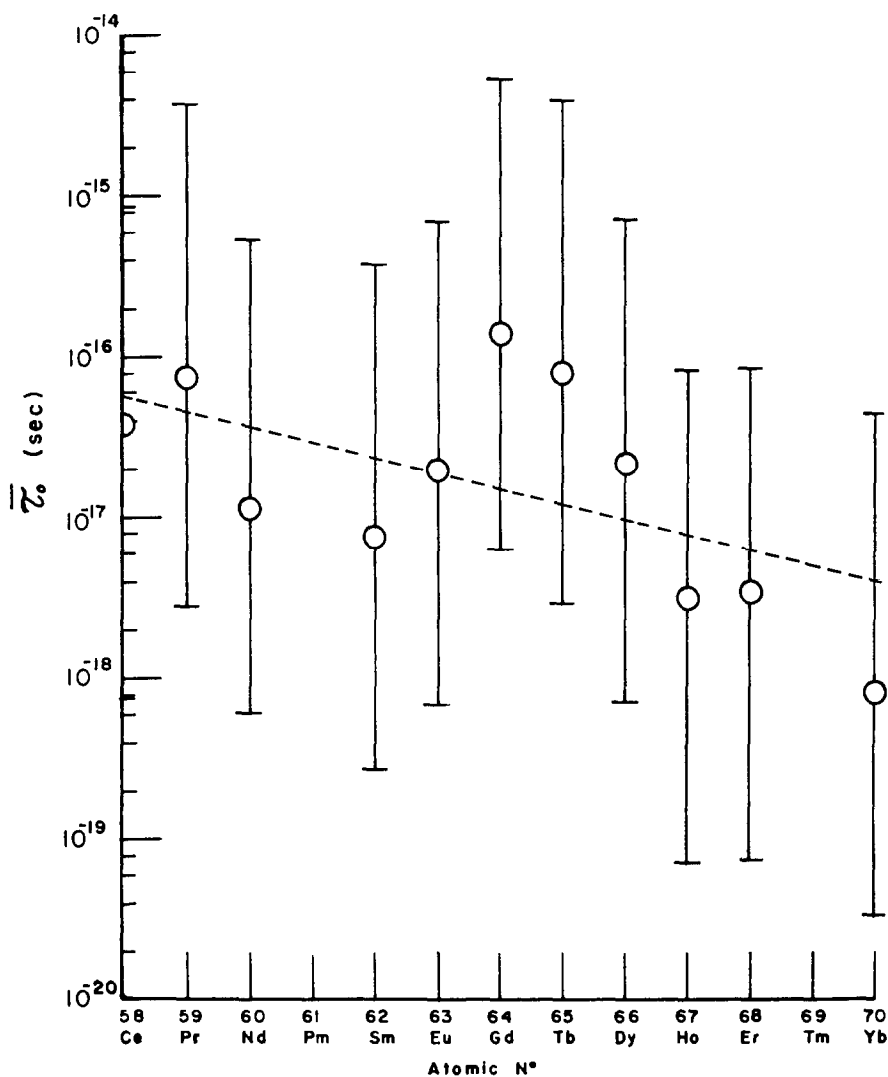
FIG. 6. Values of τ_0 as a function of atomic number of solute ions.

cause of the similarity between the collapse of the nearby anions toward a vacant site and the local distortion around the RE_{Ca}° sites, the necessary rearrangement of the normal lattice anions in connection with these two types of motion is quite analogous. One would, therefore, expect the activation energies for vacancy and interstitialcy motion in this structure to be much closer than is often the case for vacancy-interstitial combinations in other structures.

Analysis of τ_0

A comparison of the τ_0 values obtained from this work with those listed in Table I shows that the values obtained from our TDP experiments are significantly smaller. In order to properly evaluate the credibility of these values, it is necessary to examine the components which make up τ_0 and relate them to the proposed defect migration model. It can be shown that Eq. (4) can be rewritten as

$$\nu = \nu_0 \exp(\Delta S/k) \exp(-W/kT), \qquad (5)$$

where

$\nu = \tau^{-1}$ escape frequency of a fluorine ion in an interstitial position

ΔS activation entropy

ν_0 frequency of vibration of the fluorine ion

TABLE III

OBSERVED VALUES OF W, τ_0, AND N_d FOR DIFFERENT
SAMPLES

Solute	W (eV)	τ_0 (sec)	N_d (cm^{-3})
Ce	0.535	3.9 $\times 10^{-17}$	9.06 $\times 10^{17}$
Pr	0.540	7.8 $\times 10^{-17}$	1.12 $\times 10^{18}$
Nd	0.560	1.1 $\times 10^{-17}$	6.01 $\times 10^{17}$
Sm	0.540	7.8 $\times 10^{-18}$	7.58 $\times 10^{17}$
Eu	0.540	2.0 $\times 10^{-17}$	5.12 $\times 10^{17}$
Gd	0.510	1.4 $\times 10^{-16}$	7.24 $\times 10^{17}$
Gd[a]	0.500	1.49 $\times 10^{-16}$	7.06 $\times 10^{17}$
Tb	0.515	8.0 $\times 10^{-17}$	7.76 $\times 10^{17}$
Dy	0.530	2.2 $\times 10^{-17}$	3.32 $\times 10^{17}$
Ho	0.555	3.2 $\times 10^{-18}$	7.64 $\times 10^{17}$
Er	0.550	3.5 $\times 10^{-18}$	2.25 $\times 10^{18}$
Yb	0.560	8.4 $\times 10^{-19}$	5.91 $\times 10^{17}$

[a] Sample from A. D. Franklin.

It is the usual practice to assume that values of the attempt frequency, ν_0, are about 10^{13} sec^{-1}, as this is the order of the Debye frequency for normal accoustical phonon modes in a perfect lattice. It would seem more reasonable, however, to expect that the vibrational frequency of an ion in an interstitial site is greater than that of the same ion in a normal lattice site. In turn, this latter value should be larger than the vibrational frequency of an ion in the neighborhood of a vacancy. This assumption is in keeping with the more detailed analysis of Mott and Gurney (26), and Huntington et al. (27) on the entropy of formation of various types of defects. In the case of NaCl, for example, the ratio of the vibrational frequencies of a perfect crystal to that of one containing a Schottky pair is reported to be 1.32 (28). Unfortunately, no such estimate of
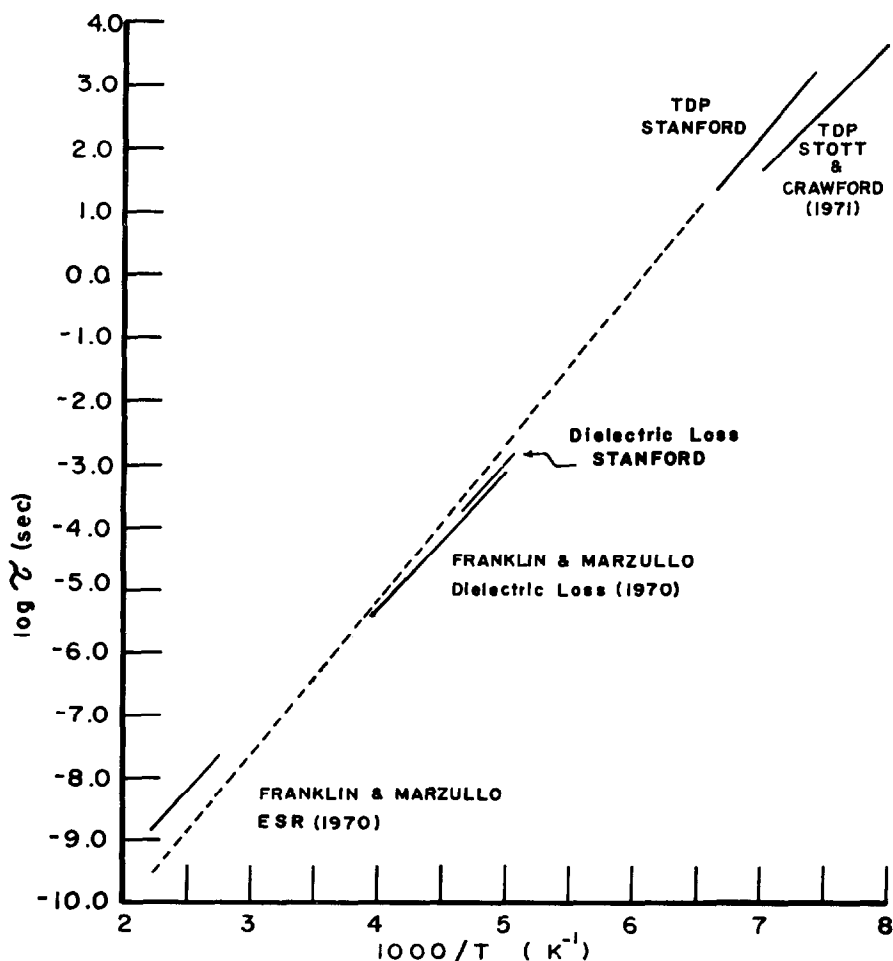

FIG. 7. Logτ versus $1/T$ for Gd-doped CaF$_2$: Values from this work extrapolated to region of published data using ESR and dielectric loss techniques, Franklin and Marzullo (9). TDP results of Stott and Crawford (10) and dielectric loss data from Stanford (18) are also shown.

the vibrational frequencies has been calculated for an isolated interstitial in polar crystals.

Recalling that ENDOR measurements have shown the trivalent solute ion and the fluorine interstitial to be closer to each other than the normal cation–anion distance, it is reasonable to expect that the vibrational frequency of the interstitial in the (nn) position is greater than that of an isolated interstitial fluorine ion. The magnitude of this difference is unknown; however, the tendency will be to contribute a different (larger) value of ν_0 to experiments which measure the kinetic parameters of bound defects in CaF_2, as is the case for TDP experiments, than those which measure the long-range motion of free interstitial ions.

An area in which cognizance has been taken of defect-related changes in vibrational frequency is that of the analysis of D_0 values in tracer diffusion experiments. This effect has been used to explain anomalously high D_0 values for diffusion in III–V compounds (29) and also to explain the normally lower values of D_0 for materials with Frenkel disorder than for those with Schottky disorder (26).

Let us next consider the entropy of activation. Ideally, we would like to be able to compute the change in entropy if an interstitial ion (or the interstitialcy pair) is moved infinitely slowly from its initial position to a saddle point configuration corresponding to the top of the free energy barrier for motion. There is no satisfactory manner of calculating the absolute value of this parameter at the present time; however, it is possible to obtain at least a feeling for the direction of the change and its relative magnitude by following the reasoning of Zener (30). The transfer of the ion must necessarily be associated with an increase in the strain energy of the crystal, which results in a lowering of the elastic modulus in the region of the defect. Zener showed that this decrease in the elastic modulus is accompanied by a positive increase in entropy, i.e.,

$$\Delta S \simeq -d(\mu/\mu_0)/d(T/T_m)\,(\Delta H/T_m), \qquad (6)$$

where μ is the shear or tensile modulus of the material. This elastic contribution to ΔS for a vacancy in metallic copper at its saddle point configuration has been calculated from first principles by Huntington et al. (27). Because of its complexity, such a calculation was not attempted for the activated state of an interstitial. However, these authors noted that the elastic contribution is expected to be of major signifi-

cance in the determination of ΔS for defects causing large distortions, as is the case for interstitialcy transport.

Zener also pointed out that the coefficient of $\Delta H/T_m$ in Eq. (6) has very nearly the same magnitude for most metals (30). The information available on the temperature dependence of the shear modulus for CaF_2 (31), SrF_2 (32), and BaF_2 (33), all of which have the CaF_2 structure and exhibit anti-Frenkel disorder, indicates that the term $d(\mu/\mu_0)/d(T/T_m)$ decreases significantly in going from CaF_2 to BaF_2. This would indicate that the entropy of activation should decrease in the same order.

Figure 6 shows that the τ_0 values obtained from this work vary from 6×10^{-17} to 4×10^{-18} sec over the series of rare earth solutes studied. If we assume that the local frequency of the interstitial ions is twice as large as the lattice frequency calculated from the Debye temperature, 9.9×10^{12} sec $^{-1}$ (1), then the values of ΔS should vary from $6.7k$ to $9.3k$. The only value of the entropy of activation of the fluorine interstitial in CaF_2 that the authors are aware of is $10.5k \pm 3.5k$ reported by Ure (1), which agrees well with these values. The corresponding values for vacancy motion reported by Ure varied from $\Delta S = 8k \pm 2k$ at low temperature (200°C) to $\Delta S = 1.25k \pm 0.5k$ at 600°C.

Bollmann et al. (4) reported values of ΔS for vacancy motion and interstitial motion in SrF_2 as $\Delta S_v = 2.4k$ and $\Delta S_i = 3.1k$, respectively. This is in the direction that one would expect, in light of the temperature dependence of the shear modulus. The lower values of ΔS_v compared to ΔS_i are also in keeping with expectations.

It should further be noted that the Debye temperature decreases progressively from 513K for CaF_2 (31) to 380K for SrF_2 (32) and 282K for BaF_2 (33). Values of ν_0 are also expected to decrease in this order, thus contributing to an increasing value of τ_0 from CaF_2 to BaF_2.

Conclusions

The kinetics of defect dipole reorientation in CaF_2 have been studied by the technique of thermal depolarization in a series of single crystals containing fixed concentrations of rare earth solute ions. The activation energy for motion of the $(RE_{Ca}^{\circ}:F_i')$ dipole can be expressed as $W = 0.53 \pm 0.05$ eV throughout the series of lanthanide rare earth solutes investigated.

This value of W is quite similar to that previously reported for the motion of fluorine vacancies, and considerably lower than values determined for the motion of fluorine interstitials on the basis of experiments involving long-range transport. Using information obtained by use of ESR and ENDOR techniques on the distortion in the neighborhood of the bound dipole, it has been shown that the energy for reorientation of the dipole pair is expected to be smaller than the energy for long-range transport of the free F_i' ion. Acceptance of the interstitialcy mechanism, combined with information about lattice distortion in these materials, lends support to the observation of comparable activation for motion of both the positive and negatively charged defects in this system.

In the particular case of Gd-doped samples, the parameters for dipolar reorientation obtained in this study can be extrapolated over 12 orders of magnitude in τ to fall within less than a factor of 10 from the results of other investigators using two different techniques.

The τ_0 values vary from 6×10^{-17} to 4×10^{-18} over the series of trivalent lanthanide solutes, according to a least-mean-square analysis of all the data. These values are considerably lower than most previously published results. The component parameters which make up the τ_0 function have been discussed, and the general practice of arbitrarily assigning the Debye frequency of a perfect lattice to a tightly bound interstitial or the loosely bound neighbors of a vacancy shown to be improper.

Zener's (30) theory of the influence of the temperature dependence of the elastic constants on the entropy of activation supports the values of τ_0 found in this work. Values of ΔS calculated from experimental τ_0 values are in good agreement with a previously published value for interstitial motion in CaF_2. Available data concerning the temperature dependence of the shear modulus in CaF_2, SrF_2, and BaF_2 are consistent with the trend to lower values of ΔS in the latter systems. The decreasing value of the Debye temperature also indicates decreasing values for ν_0, and thus increasing values of τ_0, in this series of compounds. The relative magnitudes reported for the entropy of activation of interstitials and vacancies in SrF_2 is consistent with the assumption that the local vibrational frequencies are different for these two defect types, and lends further credence to the very low τ_0 values found for interstitial transport in this work.

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