

Activation volume for interstitial motion in strontium fluoride

Carl Andeen

Physics Department, Case Western Reserve University, Cleveland, Ohio 44106

L. Michael Hayden and John Fontanella

Physics Department, U.S. Naval Academy, Annapolis, Maryland 21402

(Received 25 June 1979)

The complex dielectric constant for erbium-doped strontium fluoride has been measured at pressures up to 0.4 GPa over the temperature range 300–360 K. Consequently, the reorientation of a type-II dipole (substitutional rare-earth and next-nearest-neighbor interstitial-fluorine charge compensator) has been studied. The activation volume for the motion is found to be 4.73 ± 0.1 cm³/mol. It is argued that this value should be similar to the migration volume for “free” interstitials. Excellent agreement is found between a value for the migration volume calculated from Flynn’s dynamical-diffusion model and the experimental value for bound interstitials. Finally, the compressibility of the activation volume is found to be more than an order of magnitude greater than the compressibility of the host lattice, and the thermal-expansion coefficient for the activation volume is found to be negative.

INTRODUCTION

In recent years, there has been increased interest in interstitial and vacancy motion for the alkaline-earth fluorides. One reason is that the alkaline-earth fluorides are isomorphous with UO₂ and ThO₂, the diffusion properties for which are of practical importance. Another reason is that the alkaline-earth fluorides are fluorine-anion superionic conductors at elevated temperatures and hence the diffusion properties for those materials are of interest in themselves.

The most straightforward approach to this problem is, of course, ionic conductivity, and careful experiments have recently been carried out using this technique.^{1,2} However, useful information concerning ion motion can also be obtained by studying the motion of bound interstitials (or vacancies). A mobile bound ion (or vacancy) usually exists as the charge compensator for a substitutional aliovalent ion, and this pair of charges forms a dipole. The two techniques most often used to study such dipoles in solids are ionic thermocurrents (ITC) and dielectric relaxation (DR). Extensive studies of dipolar defects in alkaline-earth fluorides have been carried out in recent years using these techniques as exemplified by Refs. 3–9 and references therein.

The present work represents the first study of bound interstitial motion in alkaline-earth fluorides at elevated pressures. Both the activation volume for local migration and its variation with temperature and pressure are determined for the type-II dipole in erbium-doped strontium fluoride. The results are discussed by comparison with available information concerning the motion of “free” interstitials.

EXPERIMENTAL PROCEDURE

The sample studied was strontium fluoride doped with 0.1 mol % of erbium and is the same crystal as studied previously¹⁰ at zero pressure. For the present high-pressure experiments, DR techniques were used once again.

Pressures up to 0.4 GPa were generated using an Enerpac pump, and Spinesstic 38 was used as the pressure fluid. The pressure bomb and multiple sample holder were similar to that described elsewhere.¹¹ Temperatures from 300 to 360 K were achieved using an oil bath. The temperatures were measured *in situ* by monitoring the capacitance of a “pure” strontium fluoride sample which occupied one of the positions in the sample holder. The temperatures were then calculated from the capacitance since the variation of the capacitance of strontium fluoride with temperature at zero pressure is well known.^{12,13} Consequently, the absolute temperatures were only obtained when the system was at atmospheric pressure. However, the temperature was measured both at the beginning and the end of a run, and the temperature of the oil bath was monitored throughout the run. It was concluded that the stability was better than 0.1 K over the course of a run.

The pressures were measured using a CGA Model 73 capacitive high-pressure gauge¹⁴ which was connected to the system outside the temperature bath. In order to compensate for slight changes in the pressure due to leaks while the data were being taken, a short length of pressure tubing connecting the pressure sensor with the pressure bomb was heated using the pressure gauge as a feedback controller. The pressures were controlled and measured at about the 4×10^{-5}

GPa level.

The conductance divided by the frequency, G/ω , and the capacitance C were measured at each temperature and pressure using a modified General Radio 1615 bridge operating at the five audio frequencies 10^2 , $10^{2.5}$, 10^3 , $10^{3.5}$, and 10^4 Hz. The generator-detector assembly was designed to allow single knob switching between frequencies and an interface was used which gave a digital output once a manual balance was achieved. The data were taken isothermally and were converted to the complex dielectric constant at various temperatures, pressures, and frequencies,

$$\epsilon_{T,P,\omega}^* = \epsilon_{T,P,\omega}' - j\epsilon_{T,P,\omega}'' \quad (1)$$

as follows. The real part of the dielectric constant at 1000 Hz, 300 K, and 1 atm has been determined to be¹⁰

$$\epsilon_{300,1,2\pi \times 10^3}' = 6.5204 \pm 0.0006.$$

The dielectric constant at 300 K, atmospheric pressure, and frequencies other than 1000 Hz was then calculated assuming that the relative change in dielectric constant with frequency is equal to the relative change in capacitance. The real part of the dielectric constant at 1 atm and temperatures other than 300 K was then calculated from

$$\frac{\epsilon_{T,1,\omega}'}{\epsilon_{300,1,\omega}'} = \frac{C_{T,1,\omega}}{C_{300,1,\omega}} \exp\left(-\int_{300}^T \frac{\beta}{3} dT\right), \quad (2)$$

where β is the isobaric-volume thermal-expansion coefficient for pure strontium fluoride¹⁵ due to the lack of a value for rare-earth-doped material. Next, the dielectric constant at pressures other than atmospheric at each temperature was calculated from

$$\frac{\epsilon_{T,P,\omega}'}{\epsilon_{T,1,\omega}'} = \frac{C_{T,P,\omega}}{C_{T,1,\omega}} \exp\left(\int_{1 \text{ atm}}^P \frac{\chi_T}{3} dP\right), \quad (3)$$

where

$$\chi_T = \chi_{308} + \left(\frac{\partial \chi}{\partial P}\right)_T P + \left(\frac{\partial \chi}{\partial T}\right)_P (T - 308)$$

is the isothermal compressibility. The values for χ_T and its pressure and temperature derivatives are given elsewhere.¹¹ Finally, the imaginary part of the dielectric constant at all pressures, temperatures, and frequencies was calculated from

$$\epsilon_{T,P,\omega}'' = \frac{\epsilon_{T,P,\omega}' G_{T,P,\omega}}{\omega C_{T,P,\omega}}. \quad (4)$$

RESULTS AND DISCUSSION

It is known that the zero-pressure DR spectrum for erbium-doped strontium fluoride consists of

one strong peak centered at about 1000 Hz and 320 K.¹⁰ This relaxation has been attributed to a type-II dipole¹⁶ consisting of a substitutional rare-earth and next-nearest-neighbor (nnn) interstitial-fluorine charge compensator. Further evidence in support of this identification has been given recently.^{10,17,18} It is thought that the relaxation takes place via "jumps" of the nnn interstitial-fluorine ion between equivalent sites.

In the present work, it is found that the peak shifts to a higher temperature at a fixed frequency or a lower frequency at fixed temperature with the application of pressure.

Since the data were taken isothermally, it was more convenient to analyze the data at a fixed temperature and pressure by fitting the frequency data. This is, of course, the conventional technique as opposed to the procedure followed by the authors in all previous papers where the data were analyzed at fixed frequencies. The advantage of the conventional technique is that the position of the peak gives the relaxation time of the dipole, τ , directly since $\omega\tau = 1$ exactly at the peak position. This relation is only approximately true for a peak in temperature. However, the disadvantage of the conventional technique is that dispersion becomes an important uncertainty in the determination of the peak position.

In order to determine the peak position and hence relaxation time in the present work, the data for $\epsilon_{T,P,\omega}''$ vs frequency was fit to a broadened Debye peak using the Cole-Cole expression¹⁹:

$$\epsilon_{T,P,\omega}'' = \frac{(\epsilon_L' - \epsilon_H') \cos(\alpha\pi/2)}{2\{\cosh[(1-\alpha)x] + \sin(\alpha\pi/2)\}}, \quad (5)$$

where $x = \ln(\omega\tau)$ and in this case τ represents the most probable relaxation time. α is the Cole-Cole parameter and ϵ_L' and ϵ_H' are the "low-" and "high-" frequency limits of the dielectric constant where low and high mean relative to the effects of the relaxation only. Also, it is assumed that

$$\epsilon_L' - \epsilon_H' = A/T, \quad (6)$$

where A is known as the dipole strength and is proportional to the concentration and square of the dipole moment. Typical data along with the best fit to Eq. (5) are shown in Fig. 1.

It was found that for each temperature the most probable relaxation time is well represented by a polynomial of the form

$$\ln\tau = a + bP + cP^2. \quad (7)$$

The coefficients a , b , and c are listed in Table I. Typical results are shown in Fig. 2. For each temperature and pressure, the best fit value of A was 295 ± 1 K. The value of α was found to be slightly different for each temperature varying

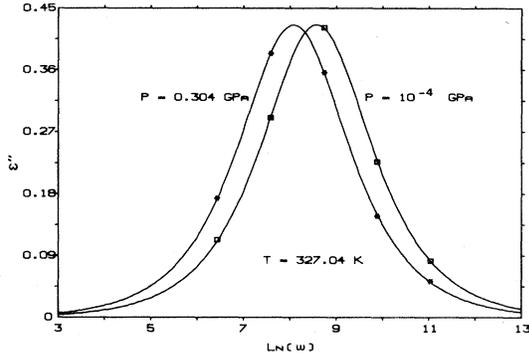


FIG. 1. ϵ'' vs $\ln(\omega)$ for type-II dipoles in 0.1 mol% $\text{SrF}_2:\text{Er}$ at 327.0 K and $P=10^{-4}$ GPa and 0.304 GPa.

from 0.037 at the lowest temperature to 0.043 at the highest. However, α did not change with pressure at a given temperature.

In addition, the 1 atm data were found to be extremely well represented by the Arrhenius equation

$$\ln\tau = \ln\tau_0 + E/kT, \quad (8)$$

where E and τ_0 are constants known as the activation energy and reciprocal frequency factor, respectively. k is Boltzmann's constant. A best fit of the data yielded the 1-atm activation parameters $E=0.701$ eV and $\tau_0=3.0 \times 10^{-15}$ s which are in excellent agreement with the zero-pressure values reported previously¹⁰ using the alternative procedure mentioned above and other apparatus. The estimated uncertainty in both E and $\ln\tau_0$ is 1.0%.

It is to be emphasized that the activation energy 0.701 eV is reasonably close to that for "free" interstitial migration in strontium fluoride which lies in the range 0.74–0.95 eV.²⁰ This is expected since, as pointed out above, this relaxation is associated with "jumps" of a nnn interstitial-fluorine ion. Consequently, the motion should be similar to that for a free interstitial since the bound interstitial is relatively far from the substitutional and hence the effects of distortion should be min-

TABLE I. Best-fit parameters describing the relaxation time as a function of pressure and the activation volume at various temperatures for type-II dipoles in erbium-doped strontium fluoride.

T	a	$b(\text{GPa})^{-1}$	$c(\text{GPa})^{-2}$	$V_m(\text{cm}^3/\text{mol})$
321.47	-8.147 89	1.77	-0.30	4.83
324.01	-8.351 17	1.72	-0.19	4.74
327.04	-8.579 91	1.67	-0.13	4.63
332.92	-9.017 28	1.67	-0.23	4.74
338.86	-9.454 94	1.65	-0.16	4.75
341.35	-9.623 15	1.61	-0.10	4.68

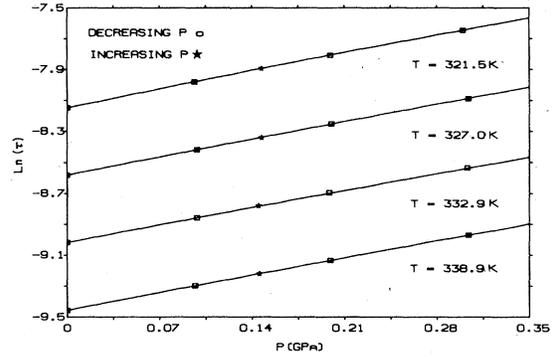


FIG. 2. $\ln(\nu)$ vs pressure for type-II dipoles in 0.1 mol% $\text{SrF}_2:\text{Er}$ at various temperatures.

imal.

The pressure results allow an evaluation of the pressure dependence of the activation parameters since

$$\left(\frac{\partial(\ln\tau)}{\partial P}\right)_T = \left(\frac{\partial(\ln\tau_0)}{\partial P}\right)_T + \frac{1}{kT} \left(\frac{\partial E}{\partial P}\right)_T. \quad (9)$$

A best fit of the data from Table I yields

$$\left(\frac{\partial E}{\partial P}\right)_T = 0.066 \text{ eV/GPa}$$

and

$$\left(\frac{\partial}{\partial P}(\ln\tau_0)\right)_T = -0.62/\text{GPa}.$$

Care must be taken in the interpretation of these results, however, since

$$\tau = \frac{1}{2\nu_{22}}, \quad (10a)$$

where a nnn–nnn jump is assumed since a nn site does not exist for erbium-doped strontium fluoride. The notation of Mathews and Crawford¹⁷ is used for the jump frequency ν_{22} along with the results of Nowick.²¹ Consequently,

$$\tau = \frac{1}{2\nu_a} \exp(g_m/kT), \quad (10b)$$

where ν_a is the frequency with which the interstitial ion approaches the energy barrier. Since

$$g_m = h_m - Ts_m, \quad (11)$$

where h_m is the migration enthalpy and s_m is the migrational entropy, it follows that

$$\tau = (e^{-s_m/k} / 2\nu_a) \exp(h_m/kT) \quad (12)$$

and E actually is h_m and

$$\tau_0 = e^{-s_m/k} / 2\nu_a. \quad (13)$$

In order to calculate the effects of pressure on the activation parameters theoretically, then, the ef-

fects of pressure on the entropy must be evaluated. Such calculations are currently in progress.²²

However, the pressure data also allow a determination of the activation volume V_m which is defined by

$$V_m = \left(\frac{\partial g_m}{\partial P} \right)_T, \quad (14)$$

which, by Eq. (10) can be calculated from

$$V_m = kT \left[\left(\frac{\partial(\ln\tau)}{\partial P} \right)_T + \left(\frac{\partial(\ln\omega_a)}{\partial P} \right)_T \right] \quad (15)$$

$$= kT(b + \chi_T \gamma_a), \quad (16)$$

where

$$\gamma_a = - \left(\frac{\partial \ln \omega_a}{\partial \ln V} \right)_T \quad (17)$$

is the approach-mode Gruneisen parameter. This quantity is not known exactly. However, the approach mode should be similar to the long-wavelength transverse-optic mode where the lattice of positive ions vibrates in antiphase with the lattice of negative ions. A similar situation has been noted for impurity-vacancy dipoles in alkali halides.²³ Consequently, it is concluded that $\omega_a \approx \omega_{TO}$ or $\gamma_a \approx \gamma_{TO}$. The existing experimental values for γ_{TO} are 1.2 (Ref. 24) and 3.1 (Ref. 25) and consequently there is considerable uncertainty in the experimental value. However, it has been shown,¹² under the assumption that the Szigeti effective charge e^* is volume independent, that $\gamma_{TO} = 2.61$. If the usual interpretation of e^* as a measure of distortion is correct, the actual value of γ_{TO} should be only slightly less than 2.61. This is consistent with a shell-model calculation of γ_{TO} for calcium fluoride and barium fluoride where values of 2.29 and 2.31 respectively are obtained.²⁶ In lieu of a reliable experimental value, it will be assumed that $\gamma_a = \gamma_{TO} = 2.6$. The values of V_m calculated on the basis of Eq. (16) are listed in Table I. From the results it is concluded that the value in the temperature range of interest is 4.73 ± 0.1 cm³/mol.

It is of interest to compare the results with the dynamical-diffusion model of Flynn²⁷ which leads to a theoretical expression for the activation volume in the form

$$V_m = 2\gamma_a \chi_T g_m. \quad (18)$$

Using Eqs. (11) and (13), Eq. (18) becomes

$$V_m = 2\gamma_a \chi_T [\hbar_m + kT \ln(2\nu_a \tau_0)]. \quad (19)$$

Using the experimental values mentioned above along with the value of ν_a (ν_{TO}) of Denham *et al.*,²⁸ Eq. (19) yields $V_m = 4.44$ cm³/mol. Thus, good agreement is obtained between the theory and the

experimental value for the motion of bound interstitials.

The data also allow a calculation of the thermal expansion coefficient of the activation volume,

$$\beta_m = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_P. \quad (20)$$

From Eq. (11), it follows that

$$T \left(\frac{\partial s_m}{\partial P} \right)_T = - \left(\frac{\partial g_m}{\partial P} \right)_T + \left(\frac{\partial h_m}{\partial P} \right)_T \quad (21)$$

$$= -V_m + \left(\frac{\partial E}{\partial P} \right)_T. \quad (22)$$

In addition, it is known that²⁹

$$\left(\frac{\partial V_m}{\partial T} \right)_P = - \left(\frac{\partial s_m}{\partial P} \right)_T \quad (23)$$

from which it is calculated that $\beta_m \approx -10^{-3}/K$. Negative thermal-expansion coefficients for activation volumes are not entirely unexpected.²⁹

Finally, the results allow a determination of the pressure dependence of the activation volume and hence a compressibility for the defect since

$$\left(\frac{\partial V_m}{\partial P} \right)_T = kT \left(\frac{\partial^2(\ln\tau)}{\partial P^2} \right)_T + \frac{\partial^2(\ln\omega_a)}{\partial P^2} \bigg|_T \quad (24)$$

or

$$= kT \left[2c + \left(\frac{\partial \chi_T}{\partial P} \right)_T \gamma_a - \chi_T^2 \frac{\partial \gamma_a}{\partial \ln V} \right]. \quad (25)$$

Only the last term is not known experimentally. However, Ruppini and Roberts³⁰ have shown theoretically that for alkali halides

$$\left(\frac{\partial \gamma_a}{\partial \ln V} \right) \approx 4.8.$$

Consequently, the last term in Eq. (25) is probably very small compared with the first term $2c$. Using a value of $c = 0.18/\text{GPa}^2$, Eq. (25) yields

$$\left(\frac{\partial V_m}{\partial P} \right)_T \approx -1 \frac{\text{cm}^3}{\text{mol GPa}}.$$

The compressibility for the migration volume is thus

$$\chi_m \equiv - \frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T \approx 0.2/\text{GPa} \quad (26)$$

and is about fifteen times greater than the bulk compressibility.

This trend is consistent with a recent calculation by Varotsos and Alexopolous³¹ who conclude that the compressibility of the migration volume of vacancies in sodium chloride is about five times that of the bulk compressibility.

SUMMARY

In summary, then, the effects of pressure on the reorientation of dipolar complexes in alkaline-

earth fluorides have been studied for the first time. The activation volume for the motion of bound interstitials is found to be 4.73 ± 0.1 cm³/mol. It is argued that this value should be similar to the migration volume for free interstitials. Good agreement is found between a value for the migration volume calculated from Flynn's dynamical diffusion model and the experimental value for bound interstitials.

Finally, the compressibility of the activation volume is found to be more than an order of magnitude greater than the compressibility of the host lattice, and the thermal-expansion coefficient for

the activation volume is found to be negative.

ACKNOWLEDGMENTS

The authors would like to thank Donald Schuele of Case Western Reserve University and C. G. Homan and T. E. Davidson of Watervliet Arsenal for their encouragement and help throughout the duration of the work. They also thank P. Varotsos of the University of Athens for helpful discussions. Finally, the authors would like to thank Fred Wasem of USNA for his efficient administrative and technical assistance. This work was supported by the U. S. Army Research Office.

- ¹D. R. Figueroa, A. V. Chadwick, and J. H. Strange, *J. Phys. C* **10**, 55 (1978).
- ²P. W. M. Jacobs and S. H. Ong, *J. Phys. Suppl.* **37**, C7-331 (1976).
- ³E. L. Kitts, Jr. and J. H. Crawford, Jr., *Phys. Rev. B* **12**, 5264 (1974).
- ⁴J. Fontanella and C. Andeen, *J. Phys. C* **9**, 1055 (1976).
- ⁵C. Andeen, D. Link, and J. Fontanella, *Phys. Rev. B* **16**, 3762 (1977).
- ⁶J. Fontanella, C. Andeen, and D. Schuele, *Phys. Rev. B* **17**, 3429 (1978).
- ⁷A. D. Franklin, J. M. Crissman, and K. F. Young, *J. Phys. C* **8**, 1244 (1975).
- ⁸A. Edgar and H. K. Welsh, *J. Phys. C* **8**, L336 (1975).
- ⁹E. Laredo, M. Puma, and D. R. Figueroa, *Phys. Rev. B* **19**, 2224 (1979).
- ¹⁰J. Fontanella, D. L. Jones, and C. Andeen, *Phys. Rev. B* **18**, 4454 (1978).
- ¹¹J. Fontanella, C. Andeen, and D. Schuele, *Phys. Rev. B* **6**, 582 (1972).
- ¹²C. Andeen, D. Schuele, and J. Fontanella, *Phys. Rev. B* **6**, 591 (1972).
- ¹³M. C. Wintersgill, J. Fontanella, C. Andeen, and D. Schuele, *J. Appl. Phys.* **50**, 8259 (1979).
- ¹⁴C. Andeen, J. Fontanella, and D. Schuele, *Rev. Sci. Instrum.* **42**, 495 (1971).
- ¹⁵A. C. Bailey and B. Yates, *Proc. Phys. Soc. London*, **91**, 390 (1967).
- ¹⁶E. L. Kitts, Jr., M. Ikeya, and J. H. Crawford, Jr., *Phys. Rev. B* **8**, 5840 (1973).
- ¹⁷G. E. Matthews, Jr. and J. H. Crawford, Jr., *Phys. Rev. B* **15**, 55 (1977).
- ¹⁸A. Edgar and H. K. Welsh, *J. Phys. C* **12**, 703 (1979).
- ¹⁹C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill, New York, 1955), p. 69.
- ²⁰P. W. M. Jacobs and A. V. Chadwick, private communication.
- ²¹A. S. Nowick, *Adv. Phys.* **16**, 1 (1967).
- ²²P. Varotsos, private communication.
- ²³J. S. Dryden and R. G. Heydon, *J. Phys. C* **11**, 393 (1978).
- ²⁴J. R. Ferraro, H. Horan, and A. Quattrochi, *J. Chem. Phys.* **55**, 664 (1971).
- ²⁵R. P. Lowndes, *J. Phys. C: Solid State Phys.* **4**, 3083 (1971).
- ²⁶R. Ruppin, *J. Phys. Chem. Solids* **33**, 83 (1972).
- ²⁷C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972).
- ²⁸P. Denham, G. R. Field, P. L. R. Morse, and G. R. Wilkinson, *Proc. R. Soc. London* **A317**, 55 (1970).
- ²⁹B. K. P. Scaife, *Complex Permittivity* (The English Universities Press Ltd., London, 1971).
- ³⁰R. W. Roberts and R. Ruppin, *Phys. Rev. B* **4**, 2041 (1971).
- ³¹P. Varotsos and K. Alexopoulos, *Phys. Status Solidi A* **47**, K133 (1978).