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Pressure and Temperature Derivatives of the Low-Frequency Dielectric Constants of the Alkaline-Earth Fluorides*

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The first- and second-order 308 °K pressure derivatives of the low-frequency dielectric constants of CaF_2, SrF_2, and BaF_2 are determined to about 0.1% and 2%, respectively. The first- and second-order 308 °K temperature derivatives are determined to about 0.2% and 20%. The results are used to calculate the associated volume derivatives. It is found that Srinivasan's calculation of $v(\partial\epsilon_s/\partial v)_T$ based on Axe's shell model agrees well with experiment. The results are also used to show that in the alkaline-earth fluorides, as in the alkali halides, the question as to the sign of the temperature-independent volume derivative of the Szigeti effective charge remains open.

INTRODUCTION

The fluorite structure of the alkaline-earth fluorides is only slightly more complex than the sodium chloride or cesium chloride structures of the alkali halides. A particularly important aspect of the difference between the alkali halides and the alkaline-earth fluorides is the lack of inversion symmetry at the anion lattice sites of the latter. This implies that under certain mechanical strains there will be internal displacements of the anions. Thus, the electrical and mechanical properties and their interrelationships for the alkaline-earth fluorides are of particular interest in the study of ionic solids. One of the most basic of the electrical properties of solids is the static dielectric constant ϵ_s. The authors have previously established[1] accurate values of ϵ_s for the alkaline-earth fluorides. The present paper contains the results for the room-temperature pressure and temperature variation of the low-frequency dielectric constant for some of the samples studied in Ref. 1.

EXPERIMENT

The apparatus and procedures used in the present experiment are the same as those described in a previous paper[2] with one exception, the pressure variation of capacitance for CaF_2. The pressure data for that crystal has been reported by the authors elsewhere[3] in a different context. In Ref. 3, a 0.01% pressure gauge is described, the reference mechanism for which is the change of capacitance of CaF_2 with pressure.

In that work eight CaF_2 pressure sensors were calibrated against a 60-ppm dead-weight pressure gauge and thus the pressure coefficients of capacitance may be derived from the data. The first- and second-order coefficients of capacitance for the eight CaF_2 samples were obtained using a procedure described later and the averaged results are listed in Table I.

The CaF_2 capacitive pressure gauge was then used in the determination of the pressure variation of capacitance for the samples measured in this work. The samples measured are some of those for which the low-frequency dielectric constants are reported in Ref. 1. They were prepared for measurement as described in Ref. 2.

RESULTS

Pressure Derivatives

Capacitance-vs-pressure data at 308 °K were obtained over the pressure range $0-3\times10^9$ dyn/cm² (10^9 dyn/cm² = 1 kbar) for an Optovac CaF_2 sample, a Harshaw and an Optovac BaF_2 sample, and two Harshaw SrF_2 samples. The results were fitted to an equation of the form

$$C/C_0 = 1 - Ap + Bp^2 \tag{1}$$

by the method of least squares. A and B are fitting parameters and p is the absolute pressure. The zero-pressure first- and second-order pressure derivatives of capacitance are then

$$\frac{1}{C_0}\left(\frac{\partial C}{\partial p}\right)_{T,\,p=0} = -A \tag{2a}$$

and

$$\frac{1}{C_0}\left(\frac{\partial^2 C}{\partial p^2}\right)_{T,\,p=0} = 2B\,. \tag{2b}$$

The resultant first- and second-order derivatives of capacitance for the Optovac CaF_2 agreed to with-

TABLE I. First- and second-order, zero-pressure, 308 °K pressure, and temperature derivatives of capacitance for the alkaline-earth fluorides.

		CaF_2	SrF_2	BaF_2
$\frac{1}{C_0}\left(\frac{\partial C}{\partial p}\right)_T$ $\left(10^{-12}\frac{cm^2}{dyn}\right)$	This work	−3.780	−4.041	−4.992
	Lowndes[a] (300 °K)	−4.37	−5.28	−5.89
	Jones[b]	−4.59 (296 °K) −3.85 (291 °K) −4.09 (323 °K)		−4.85 (298 °K) −4.89 (323 °K)
$\frac{1}{C_0}\left(\frac{\partial^2 C}{\partial p^2}\right)_T$ $\left[10^{-24}\left(\frac{cm^2}{dyn}\right)^2\right]$	This work	54.8	65.3	103
	Jones[b]	150 (296 °K) 90 (291 °K) 126 (323 °K)		80 (298 °K) 58 (323 °K)
$\frac{1}{C_0}\left(\frac{\partial C}{\partial T}\right)_p$ $(10^{-5}/°K)$	This work	26.32	22.82	23.13
	Lowndes[a] (300 °K)	24.8	24.7	24.4
$\frac{1}{C_0}\left(\frac{\partial^2 C}{\partial T^2}\right)_p$ $[10^{-7}/(°K)^2]$	This work	2.30	1.85	2.07

[a]Reference 4.

[b]B. W. Jones, Phil. Mag. 16, 1805 (1967).

in 0.2% and 1% of the respective averaged derivatives for the eight Harshaw CaF_2 samples. The Optovac CaF_2 was a bicrystal with a 300 °K dielectric constant of 6.834,[1] and the eight Harshaw CaF_2 showed dielectric constants of 6.7986 ± 0.0002. The rather large difference in the dielectric constants of the Optovac and Harshaw samples, then, is not strongly reflected in the pressure derivatives of capacitance.

The first- and second-order derivatives for the two Harshaw SrF_2 samples agreed within 0.01% and 1% of one another, which is consistent with both the uniformity of the samples as shown in Ref. 1 and the precision of the applied techniques as indicated in Ref. 3. The averaged value is listed in Table I.

Such agreement was not obtained for the BaF_2 samples in that the linear coefficient for the Optovac BaF_2 was 0.1% higher than the linear coefficient for the Harshaw BaF_2. The samples themselves are not uniform as shown in Ref. 1, and since the Harshaw sample has the lower loss, the numbers listed in Table I for the first- and second-order pressure derivatives of capacitance for BaF_2 are for the Harshaw sample only.

The values of the first- and second-order pressure derivatives of capacitance which are listed in Table I are thought to be accurate to on the order of 0.1% and 2%, respectively. The results of other workers are also listed in Table I. The agreement is not good.

Temperature Derivatives

Zero-pressure temperature-vs-capacitance data were obtained for a Harshaw BaF_2, a Harshaw and an Optovac SrF_2, and two Harshaw CaF_2. No anomalies in either the loss or the static dielectric constant were noted for the Harshaw BaF_2 or the Harshaw SrF_2. The data from 200–308 °K lent themselves particularly well to a power-series representation, and were fitted by the method of least squares to an equation of the form

$$C/C_0 = 1 + D(T - T') + E(T - T')^2 , \qquad (3)$$

where $T' = 308$ °K and T is the absolute temperature. The first- and second-order temperature derivatives were then obtained from

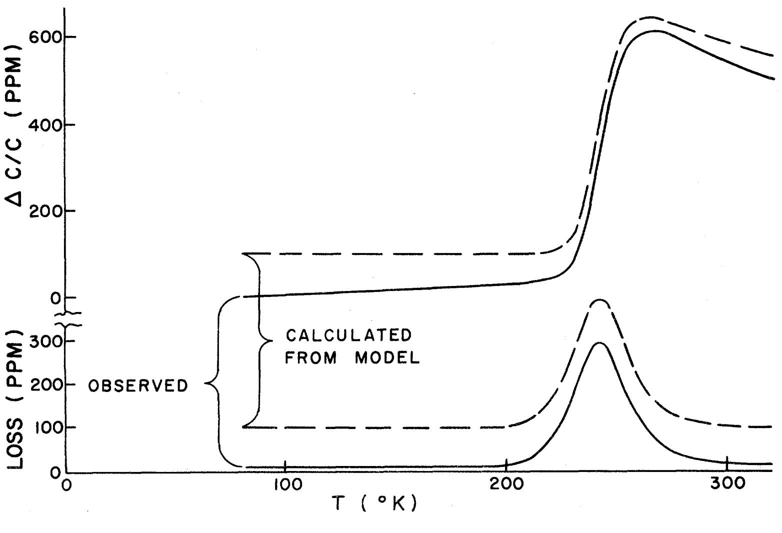

FIG. 1. Solid (dashed) line drawings represent the observed (calculated) relative difference between the Optovac and Harshaw SrF_2 samples and the observed (calculated) loss of the Optovac SrF_2. The calculated curves are displaced upward for clarity.

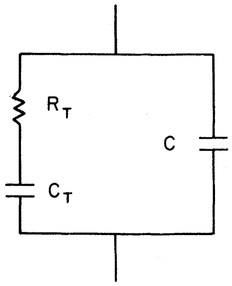

FIG. 2. Schematic model for impurity contribution to the static dielectric constant. C is the capacitance of the pure crystal, C_T represents the contribution to the capacitance from impurity orientation polarizability, and R_T represents the impurity loss mechanism. These quantities are defined quantitatively in the text.

$$\frac{1}{C_0}\left(\frac{\partial C}{\partial T}\right)_{\substack{p\\ T=T'}} = D \tag{4a}$$

and

$$\frac{1}{C_0}\left(\frac{\partial^2 C}{\partial T^2}\right)_{\substack{p\\ T=T'}} = 2E \tag{4b}$$

and the results are listed in Table I. For the Optovac SrF_2 and the Harshaw CaF_2, however, effects due to trace impurities were noted. These effects are shown in Fig. 1, where the loss for the Optovac SrF_2 and the relative difference in capacitance between the Optovac and Harshaw SrF_2 is plotted versus temperature. It is seen there that as the temperature increases, the capacitance due to the impurities increases to about half-maximum while the loss reaches a maximum. As the temperature increases further, the capacitance proceeds to a maximum, then falls off as $1/T$ and the loss decreases. (Note that the maximum capacitive aberration is only on the order of 1 part in 2000.) This sort of behavior is familiar in the study of dielectrics, being characteristic of Debye orientation polarizability. A convenient way of representing this phenomenon is through the introduction of a series resistor and capacitor which are in parallel with the intrinsic capacitance as shown in Fig. 2. On the basis of this model, the relative difference in capacitance is

$$\Delta C/C = C_T/C(1+\omega^2 R_T^2 C_T^2) \tag{5}$$

and the loss tangent is given by

$$\tan\delta = \frac{\omega C_T^2 R_T}{(C + C_T + \omega^2 R_T^2 C C_T^2)}\ , \tag{6}$$

where $\omega = 2\pi \times$ frequency; C is the capacitance of the pure crystal; $C_T = C_0 T_0/T$, which represents the contribution to the capacitance from impurity orientation polarizability; and $R_T = R_0(T/T_0)\, e^{\alpha/kT}$, which represents a loss mechanism having an activation energy α.

The quantities R_0, α, and T_0 are constants which are determined by fitting Eqs. (5) and (6) to the experimental data. The theoretical curve is also shown in Fig. 1, where the correspondence between the model and the experiment is seen to be quite good. In fact, after subtracting the theoretical curve from the experimental curve, the relative difference between the Harshaw and Optovac SrF_2 was within 100 ppm and the resultant first- and second-order derivatives for the Optovac SrF_2 came within 0.1% and 1% of the respective derivatives for the Harshaw SrF_2. The temperature results listed in Table I for SrF_2 are for the Harshaw sample only.

The above formalism is of more than academic interest, however, in that both of the CaF_2 samples studied exhibited impurity effects similar to those noted for the Optovac SrF_2. It was necessary, then, to correct the Harshaw CaF_2 for impurities, the effects of which were about one-third as large as those for the Optovac SrF_2. The results for CaF_2 after correction are listed in Table I.

The values of the first-order temperature derivative of capacitance which are listed in Table I are thought to be accurate to about 0.2%. Due to the relatively small magnitude of the second-order derivative of capacitance, it is assigned an uncertainty of 20%. Also listed in Table I is the work of Lowndes.[4] The agreement is fair.

Data Reduction

The data necessary for the transformation of the pressure and temperature derivatives of capacitance to the pressure and temperature derivatives of the static dielectric constant are listed in Table II. The values for the static dielectric constant were obtained by temperature correcting the values given in Ref. 1. The values of the isothermal compressibility χ_T, $(\partial\chi_T/\partial T)_p$, and $(\partial\chi_T/\partial p)_T$ are from the data of Wong and Schuele[5] and some unpublished data from our laboratory. The values of the volume thermal expansion coefficient γ_p and $(\partial\gamma_p/\partial T)_p$ were determined from a graphical analysis of the data of

TABLE II. 308 °K basic data used in transforming the pressure and temperature derivatives of capacitance to the various derivatives of the static dielectric constant.

	Units	CaF_2	SrF_2	BaF_2
ϵ_s		6.812	6.476	7.372
χ_T—Isothermal compressibility	$10^{-12}\ \frac{\text{cm}^2}{\text{dyn}}$	1.228	1.442	1.765
$\left(\frac{\partial\chi_T}{\partial T}\right)_p$	$10^{-17}\ \frac{\text{cm}^2}{\text{dyn}\ ^\circ\text{K}}$	40.5	51.1	69.4
$\left(\frac{\partial\chi_T}{\partial p}\right)_T$	$10^{-24}\left(\frac{\text{cm}^2}{\text{dyn}}\right)^2$	−7.48	−10.4	−15.8
γ_p—volume thermal expansion coefficient	$10^{-5}/^\circ\text{K}$	5.70	5.46	5.55
$\left(\frac{\partial\gamma_p}{\partial T}\right)_p$	$10^{-10}/^\circ\text{K}$	530	460	450

TABLE III. 308 °K, zero-pressure, first- and second-order pressure and temperature derivatives of the static dielectric constant for the alkaline-earth fluorides.

	Units	CaF_2	SrF_2	BaF_2
$\frac{1}{\epsilon_s}\left(\frac{\partial \epsilon_s}{\partial p}\right)_T$	$10^{-12}\ \frac{\mathrm{cm}^2}{\mathrm{dyn}}$	3.371	3.561	4.404
$\frac{1}{\epsilon_s}\left(\frac{\partial^2 \epsilon_s}{\partial p^2}\right)_T$	$10^{-24}\left(\frac{\mathrm{cm}^2}{\mathrm{dyn}}\right)^2$	49.4	58.2	92.2
$\frac{1}{\epsilon_s}\left(\frac{\partial \epsilon_s}{\partial T}\right)_p$	$10^{-5}/°\mathrm{K}$	24.42	21.00	21.28
$\frac{1}{\epsilon_s}\left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_p$	$10^{-7}/°\mathrm{K}$	2.03	1.62	1.84

Bailey and Yates.[6] These values were combined with the data of Table I using the equations of Appendix I of Ref. 2 to obtain the 308 °K zero-pressure first- and second-order pressure and temperature derivatives of the static dielectric constant for the alkaline-earth fluorides. These derivatives are listed in Table III.

DISCUSSION

In an analysis of the pressure and temperature derivatives of the static dielectric constant it is of value to consider the associated volume derivatives. Of particular interest in the case of the alkaline-earth fluorides are the temperature independent volume derivatives.

Temperature-Independent Effects

The temperature-independent volume-strain derivative of the static dielectric constant was calculated from

$$v\left(\frac{\partial \epsilon_s}{\partial v}\right)_T = -\frac{1}{\chi_T}\left(\frac{\partial \epsilon_s}{\partial p}\right)_T \tag{7}$$

and the results are listed in Table IV along with a theoretical calculation by Srinivasan[7] based on Axe's shell model. The agreement is relatively good; however, it should be kept in mind that Srinivasan's calculations are for the static lattice at absolute zero temperature.

The temperature-independent volume derivative can also be used to comment on Szigeti's formulation for dielectrics.[8] Szigeti has written the lattice contribution to the dielectric constant for triatomic solids as

$$\epsilon_s - \epsilon_\infty = \left(\frac{\epsilon_\infty + 2}{3}\right)\frac{Z_1 Z_2 (e^*)^2 N}{\pi \nu_t^2 \overline{M}}\,, \tag{8}$$

where Z_1 and Z_2 are the valences of the ions, $\overline{M} = 2m_1 m_2/(m_1 + 2m_2)$ is the reduced mass of the ions and the rest of the quantities are as defined in Ref. 2.

The logarithmic volume derivative of the Szigeti effective charge is then:

$$\frac{v}{e^*}\left(\frac{\partial e^*}{\partial v}\right)_T = \frac{v}{2(\epsilon_s - \epsilon_\infty)}\left[\left(\frac{\partial \epsilon_s}{\partial v}\right)_T - \left(\frac{\partial \epsilon_s}{\partial v}\right)_T\right] - \frac{v}{(\epsilon_\infty + 2)}\left(\frac{\partial \epsilon_\infty}{\partial v}\right)_T - \gamma_{\mathrm{TO}} + \frac{1}{2}, \tag{9}$$

where $\gamma_{\mathrm{TO}} = -(v/\nu_t)(\partial \nu_t/\partial v)_T$ is the transverse-optic-mode Grüneisen parameter.

The value of $(v/e^*)(\partial e^*/\partial v)_T$ is of particular interest in that it provides a clue as to the nature of e^* itself. The sign of $(v/e^*)(\partial e^*/\partial v)_T$ was studied by determining the greatest value that γ_{TO} can have in Eq. (9) before $(v/e^*)(\partial e^*/\partial v)_T$ changes sign, and the resultant values are listed in Table V as $(\gamma_{\mathrm{TO}})_{\max}$. All values of $\gamma_{\mathrm{TO}} < (\gamma_{\mathrm{TO}})_{\max}$, then, yield positive values of $(v/e^*)(\partial e^*/\partial v)_T$, which is consistent with an interpretation of e^* as a measure of ionic distortion caused by the mutual interaction of neighboring ions. The uncertainty in $(\gamma_{\mathrm{TO}})_{\max}$ is placed at about 1%. Directly determined experimental values of γ_{TO} are also listed in Table V and it is seen that while the values of Ferraro *et al.*[9] are indeed lower than $(\gamma_{\mathrm{TO}})_{\max}$, two of the three values of Lowndes[10] are higher. Thus, no conclusions should be drawn with respect to the sign of $(v/e^*)(\partial e^*/\partial v)_T$ on the basis of current data.

The second-order temperature-independent volume derivative was calculated using the data of Table II and Eq. (B2) of Ref. 2. The results of this calculation are listed in Table IV, where it is seen that this derivative is positive, showing that as the volume is decreased a given volume change has increasingly less effect on the static dielectric constant.

TABLE IV. First- and second-order temperature-independent volume derivatives and the first- and second-order volume-independent temperature derivatives of the static dielectric constant for the alkaline-earth fluorides.

	Units	CaF_2	SrF_2	BaF_2
$v\left(\frac{\partial \epsilon_s}{\partial v}\right)_T$ (expt)		18.7	16.0	18.4
$v\left(\frac{\partial \epsilon_s}{\partial v}\right)_T^{\mathrm{a}}$ (theoret.)		19.5	17.3	14.9
$v^2\left(\frac{\partial^2 \epsilon_s}{\partial v^2}\right)_T$		112	85	106
$\frac{1}{\epsilon_s}\left(\frac{\partial \epsilon_s}{\partial T}\right)_v$	$10^{-5}/°\mathrm{K}$	8.77	7.52	7.43
$\frac{1}{\epsilon_s}\left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_v$	$10^{-7}/°\mathrm{K}$	2.2	1.9	2.3

[a] Reference 7.

TABLE V. Transverse-optic-mode Grüneisen parameter and associated quantities.

	Units	CaF_2	SrF_2	BaF_2
ϵ_∞[a]		2.040	2.07	2.150
$\left(\frac{\partial n^2}{\partial p}\right)_T$	$10^{-12}\ \frac{\text{cm}^2}{\text{dyn}}$	0.697[b]	1.224[c]	1.876[b]
$(\gamma_{TO})_{max}$		2.65	2.61	2.61
$(\gamma_{TO})_{expt}$[d]		1.8	1.2	0.8
$(\gamma_{TO})_{expt}$[e]		3.2	3.1	2.4

[a] D. R. Bosomworth, Phys. Rev. 157, 709 (1967).

[b] E. D. D. Schmidt and K. Vedam, J. Phys. Chem. Solids 27, 1573 (1966).

[c] K. Vedam and Joseph L. Kirk (private communication).

[d] Reference 9.

[e] Reference 10.

Volume-Independent Effects

The first volume-independent temperature derivative was calculated from

$$\left(\frac{\partial \epsilon_s}{\partial T}\right)_v = \left(\frac{\partial \epsilon_s}{\partial T}\right)_p + \frac{\gamma_p}{\chi_T}\left(\frac{\partial \epsilon_s}{\partial p}\right)_T . \qquad (10)$$

The resultant values for $(\partial \epsilon_s/\partial T)_v$ and its associated logarithmic derivative are listed in Table IV.

It is seen that the value of $(\partial \epsilon_s/\partial T)_v$ is relatively constant for the three crystals. Since there is little variation in the dielectric constants themselves for these crystals, the results are consistent with the observation for the alkali halides that a small spread in $(\partial \epsilon_s/\partial T)_v$ is accompanied by a small spread in ϵ_s.

Finally, the second-order volume-independent temperature derivative was calculated using Eq. (B6) of Ref. 2. The cross derivative $(\partial^2 \epsilon_s/\partial p\, \partial T)$ was omitted from the calculation due to lack of data, but this term is probably positive,[4] and thus the values of the second-order volume-independent temperature derivative which are listed in Table IV should be slightly more positive. This implies that the effects of a given temperature change on the dielectric constant decrease as the temperature decreases.

CONCLUSIONS

Thus, it appears that for the alkaline-earth fluorides, as for the alkali halides, the question as to the sign of $(\partial e^*/\partial v)_T$ and hence the interpretation of e^* remains open. More accurate values of $(\gamma_{TO})_{expt}$ are necessary for the answer to this question.

In the alkaline-earth fluorides as in the alkali halides, small spreads in the quantity $(\partial \epsilon_s/\partial T)_v$ are accompanied by small differences in ϵ_s which is a further indication[2] of a correlation between $(\partial \epsilon_s/\partial T)_v$ and ϵ_s itself.

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