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Static Pockels constants p_{ij} and p_{ijk} of CaF_2 and BaF_2 under strain from *ab initio* calculations

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Ab initio results for the static (linear) elasto-optic or Pockels constants p_{ij} and (nonlinear) constants p_{ijk} for the fluorite systems CaF_2 and BaF_2 are presented from investigating the dielectric tensor under various forms and sizes of strain. The contribution to the Pockels constant p_{44} from the internal strain is important reducing the "bare" value by a factor of about 2 or more.

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I. INTRODUCTION

CaF_2 and BaF_2 are strongly ionic, wide-band-gap materials raising interest in their use for precision vacuum ultraviolet (vuv) lithography. The steadily advancing miniaturization of integrated circuits and the aim of producing microchips with increasingly small sizes needs a reduction of the wavelengths used in lithography processes from the visible to the ultraviolet ($\leqslant$400 nm) and the vacuum ultraviolet ($\leqslant$200 nm) region.[1] A demand arises for new materials for lenses with a band gap wider and transmission higher than the commonly used glassy materials.[2] In this context, CaF_2 with its large band gap is the material of choice, and BaF_2 with its similar properties constitutes an alternative material, since sizable and qualitatively good crystals can be produced. A perfect cubic symmetry is the requirement for isotropic optical properties.

For a defined optical system the knowledge of changes of the refractive index with temperature or volume is essential. Deviations of the index of refraction from the ideal ground-state value can lead to a change of quality. One issue is thereby the intrinsic birefringence induced by the spatial dispersion coming from a small optical anisotropy at nonzero energy which is studied, e.g., in Refs. 2 and 3.

Another key question is the behavior of the optical properties under strain. The thermal expansion of a material or the volume reduction due to pressure are two possible forms of strain. This aspect is the topic of the present paper. The change of the high-frequency dielectric constant, namely the elasto-optical constants, is calculated resulting from various applied strains. Despite the technological interest at vuv energies we restrict ourselves to the static Pockels constants, i.e., those at low energies compared to electronic-gap energies but high energies compared to phonon energies, and demonstrate the role of nonlinear effects.

II. NUMERICAL DETAILS

Both systems, CaF_2 and BaF_2, crystallize in the face-centered cubic fluorite structure ($Fm3m$) with three atoms in the elementary cell with the alkaline-earth ion at (0,0,0) and the F^- ions at $\pm\frac{1}{4}(1,1,1)a$.

The electronic and structural properties of the ground state have been determined within the methods of density functional theory in the local-density approximation (LDA). For the calculation of the Pockels constants we have used the pseudopotential method as implemented in the ABINIT code[4] which allows one to consider the effects of macroscopic electric fields and thus the high-frequency (low-energy) dielectric constant. Ground-state and dynamical properties have been calculated elsewhere for the sake of comparison for CaF_2 and BaF_2 with different *ab initio* program packages,[5,6] showing the reliability of the method used.

For both substances we have used the Hartwigsen-Goedecker-Hutter pseudopotential, which proved to give better dielectric and dynamical results than, e.g., Troullier-Martins or combinations of other available pseudopotentials.[5,7] For CaF_2 we have used an energy cutoff of 110 Ha and a $4\times4\times4$ **k**-point mesh leading to a precision of 10^{-3} Ha in the ground-state energy. For BaF_2 an energy cutoff of 100 Ha and the same **k**-point mesh was used. The resulting ground-state lattice constants and high-frequency dielectric constants are listed in Table I. As in many other cases the LDA result slightly underestimates the experimental value of the lattice constant and overestimates the dielectric constant, see Table I.

TABLE I. Calculated and experimental lattice constant a and equilibrium high-frequency (low-energy) dielectric constant ϵ_∞.

Method	CaF_2		BaF_2	
	a (Å)	ϵ_∞	a (Å)	ϵ_∞
Experimental (300 K)	5.463[a]	2.045[b]	6.2,[a] 6.184[c]	2.16,[b] 2.167[c]
	5.45[d,c]	2.056,[c] 2.05[e]		2.18,[e] 2.15[f]
Theoretical[g]	5.3325	2.371	6.0506	2.472

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Our neutron scattering data (10 K) (unpublished).
[e] Reference 11 (4 K).
[f] Reference 12.
[g] This work.

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III. CALCULATION OF THE POCKELS CONSTANTS

For small distortions the change in the dielectric function tensor ϵ is linear in the strain, and the (linear) Pockels constants $p_{\alpha\beta\gamma\delta}$ are defined by

$$\delta\epsilon_{\alpha\beta} \equiv \epsilon_{\alpha\beta} - \epsilon^0_{\alpha,\beta} = -\epsilon^2_\infty p_{\alpha\beta\gamma\delta} e_{\gamma\delta}, \tag{1}$$

where the Einstein summation convention is used.

In this work we investigate only the symmetrical part of the strain tensor,

$$e_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right).$$

Calculations have been performed with various finite but small strains with respect to the equilibrium structure to yield the corresponding high-frequency dielectric constants. Standard procedures include isotropic and uniaxial pressures along the cube axes for the determination of p_{11} and p_{12} and uniaxial pressures along a face or space diagonal for that of p_{44}.

We have calculated the dielectric constant for six symmetrically different strains. It should be kept in mind that the theoretical equilibrium dielectric constant is somewhat larger than the experimental one (about 15% for BaF_2 and CaF_2, see Table I). Assuming the *relative* change of the dielectric constant with strain to be realistic (the moduli of) the Pockels constants are expected to turn out to be too small by the same amount.

IV. NONLINEAR CONTRIBUTIONS

The Pockels constants will be given in the Voigt notation. For a cubic system there are three symmetrically inequivalent, nonvanishing elements of a fourth-order (linear) tensor

$$\epsilon_{xxxx} \equiv \epsilon_{11}, \quad \epsilon_{xxyy} \equiv \epsilon_{12}, \quad \epsilon_{yzyz} \equiv \epsilon_{44},$$

and nine sixth-order (nonlinear) tensor elements,

$$\epsilon_{111}, \quad \epsilon_{122}, \quad \epsilon_{112}, \quad \epsilon_{123}, \quad \epsilon_{166}, \quad \epsilon_{144},$$

$$\epsilon_{456}, \quad \epsilon_{661}, \quad \epsilon_{441}.$$

In contrast to the six sixth-order tensor elements of the nonlinear elastic constants, here relations like $\epsilon_{441}=\epsilon_{144}$ are not true since the first index refers to the derivative with respect to the electric field components, while the latter two indices refer to the derivatives with respect to strains.

Expansion in terms of the strain leads to

$$\delta\epsilon_{\alpha\beta} = \epsilon_{\alpha\beta\gamma\delta} e_{\gamma\delta} + \frac{1}{2}\epsilon_{\alpha\beta\gamma\delta\eta\zeta} e_{\gamma\delta} e_{\eta\zeta}$$

and in particular, in Voigt notation (and for symmetric strains only),

$$\delta\epsilon_1 = \epsilon_{11}e_1 + \epsilon_{12}(e_2+e_3) + \frac{1}{2}\epsilon_{111}e_1^2 + \frac{1}{2}\epsilon_{122}(e_2^2+e_3^2) + \epsilon_{112}e_1(e_2+e_3) + \epsilon_{123}e_2e_3 + 2\epsilon_{144}e_4^2 + 2\epsilon_{166}(e_5^2+e_6^2), \tag{2}$$

$$\delta\epsilon_4 = 2\epsilon_{44}e_4 + 4\epsilon_{456}e_5e_6 + 2\epsilon_{441}e_4e_1 + 2\epsilon_{661}e_4(e_2+e_3) \tag{3}$$

and cyclic.

The linear and nonlinear Pockels constants are then given by

$$\frac{d\epsilon_i^{-1}}{de_j} = -\frac{1}{\epsilon_\infty^2}(\epsilon_{ij} + \epsilon_{ijk}e_k) = p_{ij} + p_{ijk}e_k. \tag{4}$$

V. RESULTS

Rather than taking differentials we have taken differences, and thus we have been led to compute the nonlinear in addition to the linear Pockels constants. In order to obtain the single Pockels constants rather than their combinations we considered various types of strain which involve different combinations of the Pockels constants.

In general we have calculated the dielectric constant at equilibrium and two different strains (of the same symmetry); then we have fitted a parabola through these three data sets from which the linear and second-order changes can be extracted. In order to circumvent numerical noise we have used strains of the order of a percent. This may seem large, but the results for different choices of the strains turn out to be rather consistent. In fact, in almost all cases we have used the results from the different choices to estimate the numerical error bars. The results will be given in rounded numbers, even though the computations themselves have been done with a larger number of digits.

A. Strictly uniaxial strain (T_{1g} symmetry)

In this section we investigate a compression (or extension) along only one cube axis. This type of strain may be unfeasible in an experiment since it is usually accompanied by an extension (or compression) perpendicular to it; but this strain is quite interesting from a theoretical point of view since it leads to an independent and simultaneous determination of p_{11} and p_{12}.

From Eqs. (2) and (3) and with only the strain-tensor element $e_{zz}=e_3=e$ not vanishing we obtain to second order in e

$$\delta\epsilon_1 = \delta\epsilon_2 = \epsilon_{12}e + \frac{1}{2}\epsilon_{122}e^2, \tag{5}$$

$$\delta\epsilon_3 = \epsilon_{11}e + \frac{1}{2}\epsilon_{111}e^2, \tag{6}$$

$$\delta\epsilon_4 = \delta\epsilon_5 = \delta\epsilon_6 \equiv 0.$$

1. BaF$_2$

The results for BaF_2 from a quadratic fit to the results of strains $e_3=e_{zz}=\pm 0.05$ as well as with $e_3=\pm 0.2$ together with the equilibrium data ($e_3=0$) (and all other components vanishing) are very similar; the mean is

TABLE II. Calculated and experimental Pockels coefficients. The numbers in square brackets are derived values.

	Method	p_{11}	p_{12}	$p_{11}+2p_{12}$	$p_{11}-p_{12}$	p_{44}
BaF_2	Experimental[a]	0.110(11)	0.257(26)	[0.624]	[−0.147]	0.0142(14)
	Experimental[b]	[0.131]	[0.277]	[0.685]	−0.146	0.0264
	Experimental[c]				−0.152(1)	0.0251(5)
	Calculated[d]					0.113
	Calculated[e]				−0.099	0.072
	Calculated[f]	[0.0508(2)]	[0.2315(2)]	0.5139(5)	−0.1807(1)	0.02089(2)
		0.0517(6)	0.239(7)	[0.53(1)]	[−0.187(7)]	
CaF_2	Experimental[a]	0.0443(44)	0.276(28)	[0.5963]	[−0.2317]	0.0287(29)
	Experimental[b]	[0.0258]	[0.202]	[0.4298]	−0.161	0.0239
	Experimental[c]				−0.184(1)	0.0252(5)
	Experimental[g]	0.026	0.198			
	Experimental[h]	0.0558	0.228	0.5118	−0.1722	0.0236
	Calculated[d]					0.048
	Calculated[e]				−0.057	0.051
	Calculated[f]	[−0.0215(2)]	[0.1972(2)]	0.3729(4)	−0.2187(2)	0.0316(3)
		−0.022(1)	0.204(6)	[0.386(13)]	[−0.226(7)]	

[a] Reference 13, Brillouin scattering at 632.8 nm.

[b] Reference 14, calculated from piezobirefringence data at 589.3 nm cited therein.

[c] Reference 1, piezobirefringence at $E=2.269$ eV; for theoretical LDA results see the figures therein and the present remarks in Secs. V A and V F here.

[d] Reference 15.

[e] Reference 16, dipole-dipole model.

[f] *Ab initio* calculation using ABINIT, this work. Error bars are from numerical uncertainties.

[g] Reference 17, pressure dependence of refractive index.

[h] Pockels (1906) as cited in Ref. 18.

$$\delta\epsilon_3 = -0.316(4)e + 1.21(6)e^2,$$

$$\delta\epsilon_1 = -1.46(4)e + 2.19(4)e^2.$$

The derived numbers of p_{11} and p_{12} appear in Table II (without square brackets) and those of p_{111} and p_{122} in Table III. For later use in Sec. V D we note

$$\frac{1}{2}\epsilon_{111} = 1.21(6), \tag{7}$$

$$\frac{1}{2}\epsilon_{122} = 2.19(4). \tag{8}$$

The relative contribution of the nonlinearities is appreciable for the strains used in our calculations, in particular the contribution to ϵ_{11} and p_{11}.

2. CaF_2

Similarly as for BaF_2 we proceed for CaF_2. Likewise, the results from $e_3=\pm 0.2$ and ± 0.05 are very similar; the mean is

$$\delta\epsilon_3 = +0.125(8)e + 0.93(5)e^2,$$

$$\delta\epsilon_1 = -1.15(3)e + 1.91(4)e^2.$$

For later use in Sec. V D we note

$$\frac{1}{2}\epsilon_{111} = 0.93(5), \tag{9}$$

$$\frac{1}{2}\epsilon_{122} = 1.91(4). \tag{10}$$

As for BaF_2 the contribution of the nonlinearities is appreciable for the strains used in our calculations. To our sur-

TABLE III. Calculated nonlinear Pockels coefficients. The error bars result from uncertainties of quadratic fits of the dielectric numbers at various strains.

	p_{111}	p_{122}	p_{112}	p_{123}	p_{456}	p_{166}	p_{144}
BaF_2	−0.40(2)	−0.72(1)	−0.03(1)	−0.19(3)	0.106(12)	−0.1571(15)	−0.264(3)
CaF_2	−0.33(2)	−0.68(2)	+0.07(2)	−0.26(4)	0.072(6)	−0.0655(7)	−0.319(3)

prise, the sign of the value for p_{11} for CaF_2 turns out to be opposite to the experimental one. We will come back to this finding at the end of the paper.

3. Strain-induced birefringence

For the strain-induced birefringence $\epsilon_\parallel - \epsilon_\perp = \delta\epsilon_3 - \delta\epsilon_1$ we obtain the values $1.15(4)e_3$ for BaF_2 and $1.28(4)e_3$ for CaF_2. This is to be compared with the theoretical values $\approx 1.1e$ and $\approx 1.15e$, respectively, from Ref. 1 for their $K_{11}-K_{12}$ as read off their figures at $E=0$. At $E=2.269$ eV, the experimental values of Ref. 1 are 0.723(7) and 0.780(8), respectively.

B. Homogeneous strain (A_{1g} symmetry)

This case corresponds to hydrostatic conditions. For all diagonal strain-tensor elements equal ($e_{xx}=e_{yy}=e_{zz}=e$ and zero off-diagonal elements) we obtain from Eq. (2)

$$\delta\epsilon_1 = \delta\epsilon_2 = \delta\epsilon_3 = (\epsilon_{11} + 2\epsilon_{12})e + \left(\frac{1}{2}\epsilon_{111} + \epsilon_{122} + 2\epsilon_{112} + \epsilon_{123}\right)e^2. \tag{11}$$

1. BaF_2

From the lattice constants 5.9, 6.0, and 6.2 Å and quadratic fits to three different combinations of two of these with the equilibrium lattice constant 6.05 Å we find

$$\delta\epsilon_1 = -3.139(3)e + 6.9(2)e^2 \tag{12}$$

and by comparison with Eq. (11)

$$p_{11} + 2p_{12} = 0.5139(5), \tag{13}$$

$$p_{111} + 2p_{122} + 4p_{112} + 2p_{123} = -2.26(6), \tag{14}$$

while from p_{11} and p_{12} of Sec. V A above for uniaxial strain along z we find

$$p_{11} + 2p_{12} = 0.53(1)$$

in reasonable agreement (within 3%) with each other. (This latter is the number in square brackets in Table II.) This is also in agreement with the result of Ref. 1, Fig. 9, where $\delta\epsilon_1 \approx -3e$ at low energies. The nonlinear constants for the two different strain symmetries *must* differ, since they contain different combinations of the p_{ijk}.

2. CaF_2

From the lattice constants 5.33 (equilibrium), 5.3, and 5.4 Å and a quadratic fit we find

$$\delta\epsilon_1 = -2.097e + 5.078e^2 \tag{15}$$

and

$$p_{11} + 2p_{12} = 0.3729(4), \tag{16}$$

$$p_{111} + 2p_{122} + 4p_{112} + 2p_{123} = -1.81(5), \tag{17}$$

assuming a numerical error as for BaF_2, namely 0.1% for the linear and 3% for the nonlinear result, while from the data for strictly uniaxial strain along z we find

$$p_{11} + 2p_{12} = 0.386(13).$$

The linear Pockels constants from the two symmetrically different strains agree within 3%. This is also in agreement with the data of Ref. 1, Fig. 7, where $\delta\epsilon_1 \approx -2.3$ (as compared to our value of 2.1) at low energies. The nonlinear constants *must* differ as mentioned above; they will be considered further below in Sec. V E.

C. Shear strain (E_g symmetry)

This corresponds to uniaxial conditions at constant volume with pressure along a cube axis. We choose pressure along the z axis; with $e_1=e_2=-\frac{1}{2}e_3=e$ and all other components vanishing in Eq. (2) the two different components $\epsilon_1 = \epsilon_2$ and ϵ_3 have different nonlinearities,

$$\delta\epsilon_1 = \delta\epsilon_2 = (\epsilon_{11} - \epsilon_{12})e + \left(\frac{1}{2}\epsilon_{111} + \frac{5}{2}\epsilon_{122} - \epsilon_{112} - 2\epsilon_{123}\right)e^2, \tag{18}$$

$$\delta\epsilon_3 = -2(\epsilon_{11} - \epsilon_{12})e + (2\epsilon_{111} + \epsilon_{122} - 4\epsilon_{112} + \epsilon_{123})e^2. \tag{19}$$

1. BaF_2

With a strain of $e_1=e_{xx}=\pm 0.02$ (and $e_1=0$) we obtain

$$\delta\epsilon_1 = +1.103e + 9.501e^2, \tag{20}$$

$$\delta\epsilon_3 = -2.209e + 9.400e^2, \tag{21}$$

and

$$p_{111} + 5p_{122} - 2p_{112} - 4p_{123} = -3.108 \quad \text{from } \epsilon_1, \tag{22}$$

$$4p_{111} + 2p_{122} - 8p_{112} + 2p_{123} = -3.078 \quad \text{from } \epsilon_3. \tag{23}$$

The average of the linear constants is

$$p_{11} - p_{12} = -0.1807(1),$$

while the numbers of Sec. V A above yield

$$p_{11} - p_{12} = -0.187(7). \tag{24}$$

(This is the number in square brackets in Table II.) Thus the calculations with strains of the three different symmetries T_{1g}, A_{1g}, and E_g give very consistent results for the two (linear) Pockels constants p_{11} and p_{12} and their combinations. Further considerations concerning different combinations of p_{11} and p_{12} will be made in Sec. V D.

2. CaF_2

Analogously to the case of BaF_2 we obtain

$$\delta\epsilon_1 = 1.231e + 7.691e^2, \tag{25}$$

$$\delta\epsilon_3 = -2.458e + 10.317e^2, \tag{26}$$

and

$$p_{111}+5p_{122}-2p_{112}-4p_{123}=-2.736 \quad \text{from } \epsilon_1, \qquad (27)$$

$$4p_{111}+2p_{122}-8p_{112}+2p_{123}=-3.670 \quad \text{from } \epsilon_3. \qquad (28)$$

The average of the linear constant is

$$p_{11}-p_{12}=-0.2187(2), \qquad (29)$$

and the numbers from Sec. V A yield the same, although less precise result

$$p_{11}-p_{12}=-0.226(7)$$

for the linear term.

D. A_{1g} and E_g data combined

The combination of the A_{1g} and E_g data can be used to determine the constants p_{11} and p_{12}. These results enter Table II in square brackets and seem to be somewhat more precise than the directly calculated values of Sec. V A.

As a further check of consistency of the Pockels constants p_{11} and p_{12} we have investigated a strain of still another symmetry, namely with $e_1=e_2=-e_3=e$ and all other components vanishing. From Eq. (2) one has

$$\delta\epsilon_1=\delta\epsilon_2=\epsilon_{11}e+\frac{1}{2}(\epsilon_{111}+2\epsilon_{122}-2\epsilon_{123})e^2, \qquad (30)$$

$$\delta\epsilon_3=(-\epsilon_{11}+2\epsilon_{12})e+\frac{1}{2}(\epsilon_{111}+2\epsilon_{122}-4\epsilon_{112}+2\epsilon_{123})e^2, \qquad (31)$$

which can be written as

$$\delta\epsilon_1=\delta\epsilon_2=\frac{1}{3}\delta\epsilon_1^{A_{1g}}+\frac{2}{3}\delta\epsilon_1^{E_g}-\epsilon_{122}e^2, \qquad (32)$$

$$\delta\epsilon_3=\frac{1}{3}\delta\epsilon_3^{A_{1g}}+\frac{2}{3}\delta\epsilon_3^{E_g}-\epsilon_{111}e^2. \qquad (33)$$

The results from a direct computation can be compared to the results derived from the data of Secs. V A–V C. With $e=0.03$ we obtain for BaF$_2$

$$\delta\epsilon_1=-0.00561,$$

$$\delta\epsilon_3=-0.07009$$

directly and

$$\delta\epsilon_1=-0.0055(4),$$

$$\delta\epsilon_3=-0.0700(5)$$

as derived from Eqs. (7), (8), (12), (20), and (21). Likewise, we find by direct computation for CaF$_2$

$$\delta\epsilon_1=+0.00635,$$

$$\delta\epsilon_3=-0.06410,$$

and from Eqs. (15), (25), (26), (9), and (10) with $e=0.03$

$$\delta\epsilon_1=+0.0063(4),$$

$$\delta\epsilon_3=-0.0641(5).$$

For this symmetry we did not investigate other values of e since the different strains led to essentially identical results, demonstrating the consistency of the results from different strains.

E. Nonlinear T_{1g}, A_{1g}, and E_g data combined

We consider the results for the T_{2g} data p_{111} and p_{122} from Sec. V A as rather reliable, since also the linear terms are quite consistent. Taking these T_{2g} data as given independently and as granted there remain the three equations (14), (22), and (23) (in the case of BaF$_2$) from the A_{1g} and E_g data for the two constants p_{112} and p_{123}. To be on the safe side we assume an error bar of 5% for the E_g nonlinearity, somewhat larger than the 3% error bars for the A_{1g} nonlinearity. In the way described we obtain the data for p_{112} and p_{123} as in Table III for BaF$_2$ and likewise for CaF$_2$.

F. Shear strains (T_{2g} symmetry)

We have investigated two different distortions,

$$\mathbf{e}_{[111]}=e_{[111]}\begin{pmatrix}0&1&1\\1&0&1\\1&1&0\end{pmatrix}$$

and

$$\mathbf{e}_{[110]}=e_{[110]}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix},$$

for uniaxial strain along the [111] and [110] directions, respectively. To second order one has from Eqs. (2) and (3)

$$\delta\epsilon_1=\delta\epsilon_2=\delta\epsilon_3=0+(2\epsilon_{144}+4\epsilon_{166})e_{[111]}^2, \qquad (34)$$

$$\delta\epsilon_4=\delta\epsilon_5=\delta\epsilon_6=2\epsilon_{44}e_{[111]}+4\epsilon_{456}e_{[111]}^2 \qquad (35)$$

for the [111] case and

$$\delta\epsilon_1=0+2\epsilon_{166}e_{[110]}^2, \qquad (36)$$

$$\delta\epsilon_2=\delta\epsilon_3=0+2\epsilon_{144}e_{[110]}^2, \qquad (37)$$

$$\delta\epsilon_6=2\epsilon_{44}e_{[110]}+O(e_{[110]}^3), \qquad (38)$$

$$\delta\epsilon_4=\delta\epsilon_5\equiv 0 \qquad (39)$$

for the [110] case.

For BaF$_2$ and CaF$_2$ it turns out that the internal strain, i.e., the shift of the F atoms from their symmetry positions $\pm\frac{1}{4}(1,1,1)$, gives a very important contribution to p_{44}. The internal strain itself is considered in Sec. V G.

1. BaF$_2$

We have used the values ±0.025 and 0.05 (and $e=0$) for $e_{[111]}$ and $e_{[110]}$, and from three quadratic fits we find

$$\delta\epsilon_1 = -0.01(2)e_{[111]} + 5.6(1.3)e_{[111]}^2,$$

$$\delta\epsilon_6 = -0.26(1)e_{[111]} - 2.6(3)e_{[111]}^2,$$

$$\delta\epsilon_1 = +0.0005(6)e_{[110]} + 1.92(2)e_{[110]}^2,$$

$$\delta\epsilon_3 = -0.0003(13)e_{[110]} + 3.23(4)e_{[110]}^2,$$

$$\delta\epsilon_6 = -0.255(2)e_{[110]} + 0.06(6)e_{[110]}^2.$$

The values for p_{44} from the two different strains come out almost identical; the average is given in Table II.

As expected from Eq. (38), the nonlinear contribution to p_{44} for the strain along the [110] direction nearly vanishes. Also as expected from Eqs. (34), (36), and (37), the linear term of the diagonal elements $\delta\epsilon_1$ and $\delta\epsilon_3$ nearly vanishes. From the [111] data we find p_{456}, and from the [110] data we find p_{166} and p_{144}, see Table III. These [110] numbers yield

$$p_{144} + 2p_{166} = -0.578(6),$$

while the [111] results, compared with Eq. (34), are much less precise,

$$p_{144} + 2p_{166} = -0.46(11),$$

with barely overlapping error bars.

Neglecting the internal strain the values of p_{44} would be too large by a factor of between 2 and 3 for $e_{[111]}$ and of about 4 for $e_{[110]}$. More details of the internal-strain parameter will be considered in Sec. V G.

2. CaF_2

The qualitative findings for CaF_2 are similar to those of BaF_2. With the values ±0.025 for $e_{[110]}$ and ±0.025 and 0.05 for $e_{[111]}$ we find

$$\delta\epsilon_1 = -0.01(6)e_{[111]} + 3.5(1.7)e_{[111]}^2,$$

$$\delta\epsilon_6 = -0.351(5)e_{[111]} - 1.6(1)e_{[111]}^2,$$

$$\delta\epsilon_1 = +0.0005e_{[110]} + 0.737e_{[110]}^2,$$

$$\delta\epsilon_3 = -0.0011e_{[110]} + 3.592e_{[110]}^2,$$

$$\delta\epsilon_6 = -0.357e_{[110]} + 0.059e_{[110]}^2.$$

We assume an error of 1% for p_{44} from the [110] result and of about 1% for p_{144} and p_{166} as found for BaF_2.

From the [110] data we obtain

$$p_{144} + 2p_{166} = -0.450(4),$$

while from the nonlinear [111] results for $\delta\epsilon_1$ we find the less precise value

$$p_{144} + 2p_{166} = -0.31(15)$$

with overlapping error bars. Without the internal strain the values of p_{44} would be too large by a factor of about 1.8 for $e_{[111]}$ and of about 2 for $e_{[110]}$.

3. Strain-induced birefringence

For the birefringence $\epsilon_\parallel - \epsilon_\perp = \delta\epsilon_4$ induced by the [111] strain we obtain the values $\delta\epsilon_4 = -0.26(1)e_6$ for BaF_2 and $\delta\epsilon_4 = -0.351(5)e_6$ for CaF_2 (to first order in e_6). Our values are larger by factors of about 2 and 3, respectively, than the low-energy experimental values shown in Ref. 1, despite the fact that our results for p_{44} are in good agreement with the experimental data, see Table II. The theoretical and experimental values of Ref. 1 agree well for CaF_2 but differ strongly for BaF_2, even with a wrong sign. (This has led the authors of Ref. 1 to consider the internal-strain parameter as a fit parameter, see Sec. V G.)

G. Internal-strain parameter

The earth-alkaline atom at (0,0,0) is in the centrosymmetric octahedral nearest-neighbor surrounding, and the F atoms at $\pm\frac{1}{4}(1,1,1)a$ are positioned in the noncentrosymmetric tetrahedral surrounding. Except for isotropic strain or uniaxial strain along a cube axis, the F atoms are, therefore, shifted off the (homogeneously distorted) center positions under general strain, the displacement components (in units of the lattice constant a) being given as[19]

$$u_\alpha = -\frac{1}{4}\zeta_{\alpha\beta\gamma}e_{\beta\gamma} \qquad (40)$$

with the internal-strain displacement-tensor elements $\zeta_{\alpha\beta\gamma}$. For the fluorite structure 21 of the $3\times3\times3=27$ elements of the internal-strain tensor vanish, namely those with any two or more equal indices, and the six nonvanishing elements with three different indices are all equal,

$$\zeta_{xyz} = \zeta$$

(and all permutations of the indices).

It turns out that p_{44} strongly depends upon the size of the internal strain; for a numerical study of this dependence see, e.g., Ref. 1.

1. BaF_2

The z component of the internal-strain displacement off the $\frac{1}{4}(1,1,1)$ position is found to be

$$u = -0.0076 \quad \text{for } e_{[111]} = 0.05,$$

$$u = -0.0049 \quad \text{for } e_{[111]} = 0.025,$$

$$u = +0.0074 \quad \text{for } e_{[111]} = -0.025$$

for the [111] strain and

$$u = -0.012\,05 \quad \text{for } e_{[110]} = 0.05,$$

$$u = -0.006\,05 \quad \text{for } e_{[110]} = 0.025,$$

$$u = +0.006\,00 \quad \text{for } e_{[110]} = -0.025$$

for the [110] strain. The latter [110] set of data is quite consistent and leads to an internal-strain parameter of

$$\zeta = 0.482(1).$$

It seems that there are appreciable nonlinear contributions to the internal strain only in the [111] case but not in the [110] case as is also found for the nonlinear contributions to the Pockels constant p_{44}; but upon taking the average u for $e_{[111]} = \pm 0.025$ the next higher-order contributions should cancel, and the average value $\zeta = 0.49(1)$ turns out to be very close to that from the [110] strain.

The computational result of Ref. 1 is $\zeta = 0.45$; with this value, p_{44} would have the wrong sign, and the authors of Ref. 1 treated ζ as a fit parameter, reducing it appreciably in order to get close to their experimental data. A model calculation[20] gives $\zeta = 0.754$.

2. CaF_2

The findings for CaF_2 are qualitatively similar to those of BaF_2 with a quantitative difference resulting in

$$\zeta = 0.321(1)$$

for the internal-strain parameter from the [110] strain in good agreement with $\zeta = 0.29(11)$ of the [111] data set. The computational result of Ref. 1 is $\zeta = 0.31$. A model calculation[20] gives $\zeta = 0.432$.

VI. SUMMARY

A. Linear Pockels constants

The experimental values for p_{11} and p_{12} exhibit a very large scatter, in particular for CaF_2, where values for p_{11} range from 0.026 to 0.056, see Table II. These values are derived from $p_{11} + 2p_{12}$ (A_{1g}) and $p_{11} - p_{12}$ (E_g), and naturally carry error bars as the sum of both of the latter. Results from optical experiments usually carry the dependence upon the radiation frequency[1,21] and would need to be extrapolated to low frequencies if compared to our theoretical values; however, for energies much smaller than the gap energy, the optical constants vary only slowly.[22]

From different model assumptions, calculations give the combined coefficient in the range $0.428 < p_{11} + 2p_{12} < 0.591$ for CaF_2 and $0.542 < p_{11} + 2p_{12} < 0.71$ for BaF_2.[23] The results from other model calculations[15,16,24] depend strongly on the particular models used and thus seem to be not very reliable in comparison with *ab initio* calculations; the problem seems to be the correct treatment of the change of the electronic polarizability of the model ions under strain.

Comparing the results for BaF_2 with those of CaF_2 one finds the largest differences in the values of p_{11} (next to those of $p_{11} + 2p_{12}$) in theory as well as in experiment. Both p_{11} and p_{12} are larger for BaF_2 than for CaF_2, and the shear constants p_{44} and $p_{11} - p_{12}$ are smaller.

The deviation of our results for the Pockels constants from the experimental values are larger for CaF_2 than for BaF_2. The reason for the deviation cannot be found only in the use of the theoretical rather than the experimental equilibrium lattice constant; the theoretical lattice constants are smaller than either the low- or room-temperature values and disagree by 2% to 3%: For the experimental lattice constant the theoretical value of $p_{11} + 2p_{12}$ becomes even smaller than the experimental one. (All Pockels constants or their combinations refer to the theoretical equilibrium volume.) We rather assume the differences to originate from the value of the dielectric constant, which is too large by about 15%[5,6] (see also Table I) and which enters the Pockels constants quadratically. Also, as shown in Ref. 1 the use of a finer **k**-point mesh might bring the theoretical values closer to the experimental ones. Another deviation may come from using specific pseudopotentials and/or the LDA; but with the presently used pseudopotentials and the LDA the results for the phonon properties have turned out to be quite satisfying.[5,6] Thus the unexpected theoretical sign of p_{11} for CaF_2 remains unexplained at the moment.

The error bars given in our tables are merely from numerical inaccuracies due to finite strains or different symmetries of strain. What is difficult if not impossible in an experiment can be done theoretically; choosing the strain strictly along a cube axis allows one to calculate p_{11} and p_{12} independently, and the results are in good agreement with our values derived from homogeneous and general uniaxial strain (along a cube axis).

The constant p_{44} is very sensitive to the internal strain, as the position of the F ions is not given by symmetry but by energy minimization. The theoretical value of p_{44} is overestimated by a factor of typically 2 when the internal strain is not taken into account.

B. Internal-strain parameter

Shear strain along the [111] or [110] direction makes the F atoms move off their symmetry positions. Using finite strain the shift depends nonlinearly on the strain. In the [110] case the nonlinear contribution to the internal-strain displacement is only of third order, thus making the [110] strain particularly insensitive to nonlinear effects. To our knowledge, the internal-strain parameter of BaF_2 and CaF_2 is not known experimentally.

C. Nonlinear Pockels constants

The results for the nonlinear Pockels constants are collected in Table III. As expected from the similarity of the linear strain coefficients of CaF_2 and BaF_2, also the nonlinear coefficients are of similar order of magnitude. The nonlinear coefficients are generally negative except p_{456}. The strains are chosen in our calculations such that the strain tensors contain either only diagonal or only off-diagonal elements, and thus the nonlinear parameters p_{441} and p_{661} remain undetermined. To our knowledge, the nonlinear Pockels constants of BaF_2 and CaF_2 are not known experimentally.

The influence of the nonlinear terms on the calculation of the Pockels constants by taking differences rather than differentials have been found to be important in nearly all types of strain except [110]. Too small a strain might result in too high a numerical noise, and a calculation for too large a strain suffers from the nonlinearity; this has to be kept in mind in numerical treatments. To avoid this problem we extracted our data from nonlinear equations like (2) and (3).

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