Volume and pressure dependence of ground-state and lattice-dynamical properties of BaF$_2$ from density-functional methods

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We have performed an ab initio study of BaF$_2$ by employing different program packages. Ground-state and lattice-dynamical properties are obtained from ab initio density-functional theory within local-density approximation (LDA) and generalized-gradient approximation (GGA) employing pseudopotentials and plane-wave basis sets, the electronic properties also from full-potential LAPW+LMTO methods. The results for the lattice constant and the electronic gap energies agree well within the LDA and GGA. For the band structure we found a valence-band maximum in the $\Sigma$ direction in contrast to previous works. From density-functional perturbation theory we have calculated the phonon properties. Phonon dispersion curves, elastic constants, high-frequency dielectric constant, and effective charges and their volume and pressure dependence are presented. From the calculation of the anharmonic process of thermal expansion a softening of the $X'_i$ mode was found similar to that in CaF$_2$.

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I. INTRODUCTION

Despite or because of their simple structure fluorites exhibit interesting properties and find a wide range of applications. Fluorites like CaF$_2$ and BaF$_2$ are members of the simplest classes of superionic conductors with a transition to the superconducting state$^1$ at about $T_c = 1420 \text{ K}$ and $1233 \text{ K}$ and a melting temperature$^{1,2}$ of about $T_m = 1690 \text{ K}$ and $1593 \text{ K}$ (Ref. 1) for CaF$_2$ and BaF$_2$, respectively. The fast ion conduction$^7$ with conductivities of more than $100 \text{ (}\Omega \text{m})^{-1}$ is approaching those of ionic melts above a diffuse transition $T_c$ whereas ordinary solids show$^3$ a conductivity at moderate temperatures of $10^{-6}$ (\Omega m)$^{-1}$. This conductivity is associated$^4$ with a disorder of the anion sublattice and mobile defects at a temperature $T_c$ well below the general melting at $T_m$, whereas the cation lattice remains stable.$^5$ A large thermal motion is thereby associated with the anions.$^6$

CaF$_2$ is widely used as a crystalline lens material for precision VUV optics, and BaF$_2$ represents an alternative material. Further reduction of size in photolithography is limited by the cutoff wavelength of the UV transmission. A decreasing wavelength raises problems making lenses to focus the radiation. For VUV radiation the lens material of choice is CaF$_2$ and BaF$_2$, both being wide-band-gap insulators. For processing, fabrication, and application, knowledge of volume- and temperature-dependent effects inducing stress and strain in the material is important. The technological importance asks for a good theoretical characterization of the fluorites.

Thus a study of the temperature or pressure dependence of physical properties like the dielectric constant or refractive index of ionic crystals is useful in view of their optical applications. Because of its simple structure and strongly temperature-dependent effects, the fluorite system may serve as a model system for anharmonic calculations. The success of harmonic ab initio calculations is well known,$^7$ but comparison with experiments demands further quantities like pressure dependence, thermal expansion, phonon lifetimes, or the shift of frequencies with changing temperature. A full anharmonic treatment is not feasible yet, but one approach is the calculation within a sort of quasiharmonic approximation in which anharmonic effects are taken into account via the volume dependence of phonon frequencies, like performed, e.g., in Refs. 8 and 9 to study thermodynamic properties in simple monatomic systems.

In this paper, BaF$_2$ is studied as a model fluorite employing the methods of density-functional theory and density-functional perturbation theory. The results are compared with those of the previously investigated CaF$_2$.$^{10}$ The focus is put on volume- and pressure-dependent properties. With the study of the ground-state and lattice-dynamical properties we want to add to the understanding of the perfect crystal and the anharmonic effects of lattice expansion and compression. As fluorites show huge anharmonic effects (like in CaF$_2$),$^{10}$ one can discriminate the thermal-expansion effects from the other anharmonic processes of an experiment by a calculation of volume-dependent properties.

BaF$_2$ crystallizes at ambient pressure in the cubic fluorite structure (Fm$3m$) made up of three interpenetrating fcc lattices with three atoms in the unit cell with Ba at (0, 0, 0) and F at $\pm(1/4, 1/4, 1/4)a$ (see Fig. 1), with $a$ being the lattice constant. Like CaF$_2$, BaF$_2$ undergoes a first-order phase transition at room temperature (RT) from the fcc structure to an ortho-

FIG. 1. (Color online) Crystal structure of BaF$_2$. The cube contains four formula units.
rhombic $\alpha$-PbCl$_2$-like structure at high pressures. This transition occurs in CaF$_2$ at about 8 GPa (Ref. 11) and for BaF$_2$ somewhat lower at about 3 GPa (Refs. 12 and 13). With increasing pressure a second crystallographic transformation occurs to a hexagonal phase at about 12 GPa. Metallization is found at about 33 GPa. The frequencies of phonon modes increase with increasing pressure, and therefore also $T_\text{m}$ increases.\textsuperscript{14}

BaF$_2$ shows ionic conductivity higher than that in CaF$_2$.\textsuperscript{3} The idea exists that the sublattice disorder is more extended in BaF$_2$ than in CaF$_2$ close to $T_\text{m}$ because of the different cation radius.\textsuperscript{15} Defects, hopping, and strong lattice anharmonicity seem to be characteristic of superionic conductors.

II. \textit{Ab initio} Methods

The calculations of the electronic and dynamical properties have been performed in the framework of density-functional theory (DFT) by employing different program packages within the local-density (LDA) and generalized-gradient (GGA) approximations. The pseudopotentials have been taken from the ABINIT\textsuperscript{16} and VASP\textsuperscript{17} databases.

The lattice-dynamics calculations have been done with the linear-response approach (see, e.g., Ref. 7), implemented in the ABINIT program.

The ABINIT code gives direct access to various response functions that are second derivatives of the total energy with respect to different perturbations like phonon displacements or a static homogeneous electric field. The physical properties connected with respect to these perturbations are the phonon dynamical matrices, the dielectric tensor, and the Born effective charges.

With changing the volume and in this way simulating the thermal-expansion and pressure dependence we have obtained different physical properties like volume-dependent phonon frequencies or the related mode-Grüneisen parameters and the volume dependence of the elastic constants as well as of the high-frequency dielectric constant and of the Born effective charges.

III. Ground-State Results

A. Numerical details with application to the lattice constant

For the sake of comparison and testing, the lattice parameter has been calculated with different program packages and pseudopotentials. The WIEN97\textsuperscript{18} code is an all-electron code, while the other codes are based on \textit{ab initio} pseudopotentials; e.g., the ABINIT and VASP codes employ plane-wave expansions.

Within ABINIT the calculations were done with the Hartwigsen-Goedecker-Hutter\textsuperscript{19} (GHG) pseudopotential for the Ba and F atoms. Semicore electrons assure a correct electronic response, since in view of the application to phonon properties, Ba loses all its valence electrons and the core electrons should dynamically arrange themselves as a function of phonon modes, which would be impossible in a frozen-core approximation. With this pseudopotential static and dynamic properties are well reproduced (see Secs. III B and IV A). Although GHG pseudopotentials demand a higher energy cutoff than, e.g., Troullier-Martins\textsuperscript{20} (TM) pseudopotentials, they proved to give better and more reliable results for fluorites.\textsuperscript{10,21}

A Goedecker-Teter-Hutter\textsuperscript{22} (GTH) or a TM pseudopotential for the F atom generates nearly no change in phonon frequencies, calculated for the HGH lattice constant, whereas a change of frequencies only in the range of 1%–2% is reached when a Teter (Te) pseudopotential for the Ba atom is employed, and a deviation of more than 20% in frequency appears when a TM pseudopotential for Ba is used, independent of the pseudopotential used for the F atom.

The lattice constant has been determined from the numerical minimum of the total energy. Figure 2 shows the convergence behavior of the ground-state lattice constant in the LDA for different \textit{k}-point grids and as a function of the cutoff energy.

For the subsequent calculations we have chosen a $4 \times 4 \times 4$ special \textit{k}-point grid and a cutoff energy of $E_{\text{cut}} = 100$ Ha, resulting in $a = 11.343 \text{Å}_{\text{Bohr}} = 6.05$ Å.

In VASP a cutoff energy of 1000 eV has been used in the LDA, 1400 eV in the GGA, and a $4 \times 4 \times 4$ special \textit{k}-point grid. In WIEN97 a dependence of the lattice constant upon the muffin-tin radius appeared in the 0.1% range. With increasing muffin-tin radius also the lattice constant becomes enlarged. In contrast to CaF$_2$ with nearly equal ionic radii of Ca and F, these are in a proportion of 1:1.3 in BaF$_2$. In the all-electron calculation a muffin-tin radius of $2.4 \text{Å}_{\text{Bohr}}$ for F and $2.4 \text{Å}_{\text{Bohr}}$ for Ba has been used.

The calculated lattice constants from different approaches and programs are listed in Table I together with other calculated and experimental values. The results of the different calculations in the LDA coincide quite well and likewise those in the GGA, but as already seen in CaF$_2$ and many other cases, the LDA underestimates the value of the experimental lattice parameter by a few percent and the GGA overestimates it. The calculation with CRYSTAL98, in which the method of linear combination of atomic orbitals (LCAO) is used, gives the largest lattice constant in the LDA as well as in the GGA, even if not as large as the Hartree-Fock (HF)
TABLE I. BaF$_2$: calculated and experimental lattice constants $a$ (in Å). PW and PBE stand for the PW and PBE versions of the GGA.

<table>
<thead>
<tr>
<th>Method</th>
<th>LDA</th>
<th>PW</th>
<th>PBE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABINIT (HGH)</td>
<td>6.05</td>
<td></td>
<td></td>
<td>Present</td>
</tr>
<tr>
<td>ABINIT (Te and TM)$^a$</td>
<td>6.095</td>
<td>6.26</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>VASP (PW)</td>
<td>6.094</td>
<td>6.279</td>
<td></td>
<td>Present</td>
</tr>
<tr>
<td>Wien97</td>
<td>5.990</td>
<td>6.251</td>
<td>6.265</td>
<td>Present</td>
</tr>
<tr>
<td>Wien97</td>
<td></td>
<td></td>
<td>6.233</td>
<td>24</td>
</tr>
<tr>
<td>(HSC)-Psp.</td>
<td>5.929</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Crystal98 (LCAO)</td>
<td>6.32</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>Crystal98 (LCAO)</td>
<td>6.130</td>
<td>6.292</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>TB-LMTO</td>
<td>6.09</td>
<td></td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>OLCAO</td>
<td>6.20</td>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Expt. (300 K)</td>
<td>6.2</td>
<td></td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>Expt. (300 K)</td>
<td>6.2</td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Expt. (295 K)</td>
<td>6.184</td>
<td></td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$Te for Ba, TM for F.

calculation$^{31}$ with $a=6.35$ Å. The calculation$^{25}$ with Hamann-Schlüter-Chiang$^{32}$ (HSC) pseudopotentials gives the smallest value, similar to CaF$_2$. VASP features the fastest performance but results in a relatively large lattice constant.

The deviation of the lattice parameter calculated in the LDA from the experimental one is similar to the one in CaF$_2$ ($a_{\text{exp}}=5.463$ Å, $a_{\text{theory}}=5.33$ Å), a bit more than 2%. Because of thermal-expansion effects, the theoretical lattice constant should be smaller than the room-temperature value. The extrapolation of the experimental data to low temperatures should agree with the theoretical harmonic value.

From the overall good agreement and the accordance between pseudopotential and all-electron methods the pseudopotentials used in the following seem reliable.

B. Electronic band structure

The electronic band structure and corresponding density of states have been calculated with Wien97 and are shown in Fig. 3. The uppermost valence bands, shown here, originate from 2$p$ states of the F atom. Further below, not shown here, are $p$ states of Ba. The shown part of the conduction bands are $d$ states of Ba, in agreement with experimental results and other calculations.$^{26,33}$ This is reasonable if one bears in mind that during the formation of ionic crystals electrons of the alkaline-earth atom are transferred to the $p$ states of the halogen atom. Fully occupied $p$ states of the anion dominate the valence band; the excited cationic states are in the conduction band.

Band-structure calculations for BaF$_2$ are rare, and the results are not quite clear. Our band structure as shown in Fig. 3 has been calculated within the LDA with similar results in the GGA. With the atoms in CaF$_2$ closer together than in BaF$_2$ the bands are narrower in the latter material: The valence band in BaF$_2$ is about half as wide as in CaF$_2$ and likewise the three-peak structure of the DOS originating from the first four states of the conduction band. Further above, the band structures from different calculations differ from each other, like in CaF$_2$. For example, Ching et al.$^{28}$ found the upper valence band as nearly dispersionless.

The DOS of the valence band below the Fermi energy from tight-binding methods$^{34}$ is in good qualitative agreement with the one from this work; only the width of the band is smaller.

Like in CaF$_2$ we have obtained an indirect gap. The conduction-band minimum is at the $\Gamma$ point, and the maximum of the valence band lies in the $\Sigma$ direction near $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$, while in CaF$_2$ it is at the $X$ point. (In Ref. $^{24}$ the valence-band maximum was found in the $\Delta$ direction, probably only because the $\Sigma$ direction was not investigated.) With decreasing lattice constant the gap energies increase. The gap energies are listed in Table II.

The experimental band-gap energy of about 10 eV is a bit smaller than that in CaF$_2$, where a gap between 11 and 12 eV resulted. The calculated values of the band gap do not deviate much from each other, but as is well known, in the LDA the gap is underestimated compared to experiment. From an LCAO method with Crystal98, which is based on the Hartree-Fock method, the gap energy is overestimated by far ($\approx 20$ eV) and results also in a qualitatively different band structure.$^{31}$

IV. HARMONIC-PHONON RESULTS

A. Phonon dispersion curves

With three atoms in the unit cell of BaF$_2$ one expects nine branches. The transverse modes in the [001] and [111] direction are degenerate; no degeneracy exists along [110]. The lattice dynamics has been investigated by Hurrell and Minkiewicz$^{40}$ with inelastic neutron scattering at room tem-
Table II. Direct and indirect gap energies (in eV). The conduction-band minimum is generally at $\Gamma$, but in Ref. 28 it is found at $X$.

<table>
<thead>
<tr>
<th>Method</th>
<th>Direct</th>
<th>Indirect</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wien97 (LDA)</td>
<td>6.7</td>
<td>7.197 (in $\Sigma$)</td>
<td>This work</td>
</tr>
<tr>
<td>Wien97 (GGA-PW91)</td>
<td>7.197</td>
<td>7.097 (in $\Sigma$)</td>
<td>This work</td>
</tr>
<tr>
<td>Wien97 (GGA)</td>
<td>6.97 (in $\Delta$)</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>TB-LMTO (LDA)</td>
<td>7.033 (in $Z$)</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>TB-LMTO</td>
<td>6.37 (?)</td>
<td>6.37 (?)</td>
<td>35</td>
</tr>
<tr>
<td>DFT-LCAO</td>
<td>7.5</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>OLCAO (LDA)</td>
<td>7.19 (at $X$)</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>CRYSTAL98 (LCAO)</td>
<td>$\approx$ 20</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>OPW</td>
<td>10.12</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Reflection (300 K)</td>
<td>11</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>Absorption (300 K)</td>
<td>9.06</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Reflection and abs. (78 K)</td>
<td>10.59</td>
<td>39</td>
<td></td>
</tr>
</tbody>
</table>

For our calculations a cut off energy $E_{\text{cut}}$ of 100 Ha and a special $k$-point mesh of $4 \times 4 \times 4$ have been used, as in the calculation of the lattice constant.

The results of Ref. 23 for the dispersion in the $\Delta$ and $\Sigma$ directions show good quantitative agreement with ours, but because of their use of a $2 \times 2 \times 2$ $k$-point mesh, the optical modes deviate appreciably; in their coarse DOS, some of the main features are reproduced, but the tetrahedron method used in our case gives a much more detailed result.

In Table III a comparison is made of our calculated $\Gamma$-point frequencies with some experimental values. The LO frequencies from infrared (IR) measurements were obtained from the Lyddane-Sachs-Teller (LST) relation \(^{44}\) or from the Berreman technique \(^{45}\) and compare reasonably well with each other and with other results. Also, reflectivity measurements \(^{43}\) at low temperatures (5 K) together with a finding at 4 K cited in Ref. 42 resulted in higher frequencies and come closest to our calculated harmonic values as it should be.

A shell-model calculation of frequencies at the main symmetry points gives a maximum deviation of about 10% for lower frequencies and good agreement for higher frequencies. \(^{47}\)

A comparison with the results for CaF$_2$ (Ref. 10) shows that because of the same fluorite structure, the branches result in a comparable picture. As the Ba atom is heavier than Ca, the one-phonon spectrum ranges in BaF$_2$ only up to 46 meV whereas in CaF$_2$ it extends up to 60 meV, and the elastic constants are smaller in BaF$_2$ as compared to those of CaF$_2$.

Table III. BaF$_2$: theoretical and experimental optical $\Gamma$-point frequencies (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$\omega_{\text{TO}}$</th>
<th>$\omega_{\text{LO}}$</th>
<th>$\omega_{\text{Raman}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABINIT</td>
<td>199.34</td>
<td>351.46</td>
<td>252.03</td>
<td>Present</td>
</tr>
<tr>
<td>IR, 80 K</td>
<td>$\approx$ 190</td>
<td>$\approx$ 349</td>
<td>$\approx$ 257</td>
<td>23</td>
</tr>
<tr>
<td>IR, 4 K</td>
<td>193</td>
<td>346</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>IR refl., 5 K</td>
<td>190</td>
<td>346</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>IR refl., 300 K</td>
<td>187.5</td>
<td>344</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>IR refl., 300 K</td>
<td>184</td>
<td>326</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Raman and IR, 300 K</td>
<td>189</td>
<td>330</td>
<td>241</td>
<td>45</td>
</tr>
<tr>
<td>Raman, 300 K</td>
<td>326</td>
<td>242</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) BaF$_2$: Right: phonon dispersion curves from inelastic neutron scattering (data points with thin connecting lines) at room temperature (Ref. 40) and from ab initio theory (thick lines). Triangles denote longitudinal, squares transverse polarization. The three lightly colored branches show modes which were not visible in the scattering geometry of the experiment. Left: phonon density of states from ab initio theory.
CaF$_2$ resulting in a smaller slope of the acoustic branches. Also, the optic branches show a lesser curvature. With the lattice constant calculated to be somewhat too small in the LDA, the theoretical frequencies are generally slightly too large, independent of the different pseudopotentials used.

Another difference is that the $\Delta_2$ mode in BaF$_2$ is not the lowest frequency at the zone boundary ($X_2'$) but meets the LA mode [$\Delta_1(A)$]. The highest mode along the $\Sigma$ direction does not drop as much, like also shown in the shell-model calculation by Hurrell and Minkiewicz. And at the $L$ point a clear gap between the $\Lambda_3(02)$ and $\Lambda_1(02)$ modes shows up, because of lesser curvature of the $\Lambda_3(02)$ modes, while in CaF$_2$ both modes could not be resolved. The theoretical results show good agreement with the experimental data of Hurrell and Minkiewicz; minor deviations exist only at the $L$ point, especially of the $\Lambda_3(02)$ and $\Lambda_1(01)$ modes.

### B. Phonon eigenvectors

A look at the eigenvectors shows that in the $\Delta_2$ modes only the F$^-$ ions move whereas the Ba$^{2+}$ or Ca$^{2+}$ ions are at rest for the whole $[100]$ direction. At the X point in this mode both F$^-$ ions move parallel along a cube axis $[100]$. At the $\Gamma$ point this is the threefold-degenerate Raman mode. The IR-active mode is LO-TO split. This splitting appears to be smaller in BaF$_2$ than in CaF$_2$ because of the larger reduced mass (see Sec. IV A).

In the $X_1$ mode both F$^-$ ions move antiparallel, again along a cube axis. At the $L$ point the F$^-$ ions move parallel only in the $\Lambda_3(01)$ and $\Lambda_1(02)$ modes.

### C. Elastic constants

A cubic crystal features three independent elastic constants, $c_{11}$, $c_{12}$, and $c_{44}$. The elastic constants have been obtained from the slopes of the acoustic branches along the three main-symmetry directions. The constants $c_i' = \frac{1}{2}(c_{ii} + c_{ij} + c_{jk})$ and $c_i'' = \frac{1}{2}(c_{ii} - c_{12})$ are the longitudinal and one of the shear constants for wave propagation along $[110]$, the other being $c_{44}$.

Table IV shows calculated and experimental results for the elastic constants in BaF$_2$.

Our LDA calculations agree well with the findings from other methods using the LDA. However, the elastic constants are overestimated in the LDA calculations, particularly $c_{12}$, where one of the reasons is the theoretical lattice constant being smaller than the experimental one, see Table I.

Since the theoretical results for the elastic constants do not contain temperature effects, they should be compared to experimental low-temperature data. Extrapolation of the room-temperature data from the ultrasonic pulse-echo technique to $T=0$ K leads to values larger by about 10% for $c_{11}$ and $c_{12}$, while $c_{44}$ seems to remain rather constant.

Neither in a rigid-ion nor in a shell-model can the elastic constants be reproduced properly; introduction of three-body interactions into a shell-model improves the fit.

### V. RESULTS FOR THE PRESSURE AND VOLUME DEPENDENCE

#### A. Volume dependence of phonon frequencies

A homogeneous lattice contraction can be achieved with isotropic external pressure, while an expansion is usually due to thermal expansion. Actually, the latter effect is always accompanied by additional temperature-dependent anharmonic processes, to lowest order the two-phonon decay process and that of the coupling to thermal fluctuations. These latter effects can be treated only with explicit knowledge of the anharmonic coupling constants of third and fourth order, the calculation of which would be very much involved. However, the effect of homogeneous strain can be simulated simply by starting the computations from different lattice constants.

To lowest order of perturbation theory, the change of the lattice constants or of the (squared) phonon frequencies is proportional to the strain, and to lowest order the strain is proportional to the stress.

The first-order differentials of phonon properties have been calculated from differences taken for three different lattice constants $a=5.9$, 6.05, and 6.0 Å with $a=6.05$ Å being the relaxed lattice constant. In order to check for nonlinearities calculations have been performed for lattice constants in the range from $a=6.2$ to $a=6.8$ Å. (Actually, using thermal-expansion data of Ref. 56 melting occurs at an increase of the lattice constant of about 3%—i.e., near $a=6.2$ Å.)

As experimental results for the temperature-dependent dynamics for BaF$_2$ are not available (except for the modes with $q=0$), a comparison is made mostly with theoretical results for the chemically and structurally related fluorite CaF$_2$.

#### I. $\Gamma$- and $X$-point modes

While in first-order perturbation theory the shift of the squared frequencies depends linearly on the change of the...
At $a=6.55$ Å the transverse $\Delta_2(\bar{A})$ branch becomes imaginary, at $a=6.6$ Å the $X'_2$ mode lies below the TA mode ($X'_3$), and at $a=6.8$ Å the $\Delta_3(O1)$ and $\Delta_3(O1)$ frequencies are imaginary.

With increasing lattice constant all modes at the $X$ point soften in account of weakened forces (this is similar to the case of CaF$_2$). The rates of weakening of the lower-frequency modes differ from each other leading to various mode crossings. Critical softenings occur beyond melting (neglecting further anharmonic processes, which contribute to the phonon frequencies). This is different from the mode softening due to the double-well potentials in ferroelectrics, where the rate of weakening of the soft mode is very different from that of the other modes.

The slopes of the curves in Fig. 5 for BaF$_2$ are similar to the corresponding slopes in CaF$_2$ (see Fig. 12 in Ref. 10). This is a hint at the possibility that the anharmonicity is similar in these two systems and, consequently, that the behavior of the $X$-point modes in BaF$_2$ is properly described by just the anharmonic process of thermal expansion, while further phonon-phonon processes contribute to the temperature shift of the $\Gamma$-point frequencies.

Also similar is the deviation from the linear $\omega^2$ vs $a$ behavior because of further anharmonic contributions. Therefore, we believe that many conclusions concerning the anharmonic effects in BaF$_2$ can be taken from those in CaF$_2$.

2. $X'_2$ mode

The displacement pattern of the $X'_2$ mode describes out-of-phase moving neighboring chains of $F^-$ ions in a rigid cation lattice. In BaF$_2$ and CaF$_2$ the $X'_2$ mode becomes critically soft at nearly the same difference from the equilibrium lattice constant (0.43 in CaF$_2$ and 0.49 Å in BaF$_2$ and 0.3 and 0.34 Å in comparison to the experimental lattice constant). The critical softening of the $X'_2$ mode indicates an instability of the lattice against building of a superstructure. However, melting seems to occur before critical softening.

Similar to our results, Makur and Ghosh obtained with model calculations for BaF$_2$ a softening of the $X'_2$ mode occurring above $T_a$ and at higher temperatures than in CaF$_2$ where full softening is achieved below $T_a$ (unlike in Ref. 10). Model potentials showed the softening of the $X'_2$ mode at about $T_c$ in CaF$_2$. This softening was also found in calculation for SrF$_2$ and seems to constitute a specialty in fluoride systems, since it does not occur in normal ionic crystals like NaCl.

The softening of the $X'_2$ mode at increasing volume has been claimed to be connected to the transition to the superionic state of the fluorite system. This softening is connected to reduced restoring forces acting on the displaced $F^-$ ions. Then in the superionic phase there is a negligible resistance to perturbations of (collective) $\Delta_2$-symmetry modes. But the reduced barriers may also support individual $F^-$ hopping and may thus lead to more mobile anions.

This picture is also supported by neutron powder diffraction experiments at high temperatures where the thermal motion of the anions is found to be much larger than that of the cations for $T=0$. Also, experimental anion mean-square displacements in fluorites like CaF$_2$ and BaF$_2$ are found to be

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**FIG. 5.** (Color online) The theoretical volume dependence of the squared mode frequencies at the $\Gamma$ and $X$ points showing the (general and successive critical) softening of various modes as well as the nonlinear dependence. The $X'_2$ mode, where only the $F$ ions move and the acoustic $X_3$ and $X'_3$ mode frequencies are plotted in different colors for clarity. The labels of the modes are the same as those in Fig. 4.
higher temperatures[/H20849] displaced from their regular sites, but since the anion ure[6] shows the Grüneisen dispersion of all modes along the Ref. 10[/H9004] notably the especially the,[61] though a bit less in BaF2 than in CaF2. The branches[57] consist of interstitials, anion vacancies, and surrounding relaxed atoms.[64–66]

3. Mode-Grüneisen dispersion

While having looked so far only at the Γ- and X-point modes, we will now look at the other modes. In first-order perturbation theory the shift of the squared frequencies is proportional to the change of the lattice constant a. This relation is given by the mode-Grüneisen parameters

\[ \gamma_\lambda = -\frac{d \ln \omega_\lambda}{d \ln V} = \frac{1}{6} \frac{d \ln \omega_\lambda}{d \ln a}. \] (1)

From the volume dependence of the frequencies we have calculated the mode-Grüneisen parameters (1) for BaF2. Figure 6 shows the Grüneisen dispersion of all modes along the [001](Δ) and [111](Λ) directions.

A comparison to the Grüneisen dispersion of CaF2 (see Ref. 10) shows a similar picture with some exceptions. Especially the \(\Delta_3\) modes exhibit the same striking behavior in BaF2 as in CaF2 and have the highest value at the ZB, even though a bit less in BaF2 than in CaF2. The branches \(\Delta_3(02),\ \Delta_1(\Lambda),\ \text{and}\ \Delta_1(0)\) show also the same tendency as in CaF2 even if their slopes are bigger there. The modes \(\Delta_2(\Lambda)\) and \(\Delta_2(01)\) show especially at the ZB a different behavior. In CaF2, \(\gamma_{\Delta_2(01)}\) decreases at the ZB and \(\gamma_{\Delta_2(\Lambda)}\) increases strongly; in BaF2, both decrease slightly.

In the Δ direction, the range of parameters is comparable to that in CaF2, but CaF2 gives smaller values at the zone center, e.g., for the \(\Delta_3(\Delta)\) mode which starts at 0.75 in CaF2 and at 1.2 in BaF2. And in BaF2 the \(\Delta_3(\Lambda)\) mode shows a stronger curvature towards lower values.

In the Λ direction the modes \(\Delta_3(\Lambda),\ \Delta_3(02),\ \text{and}\ \Delta_3(01)\) result in a behavior similar to the one in CaF2. Especially the modes \(\Delta_1(\Lambda)\) and \(\Delta_1(01)\) in CaF2 feature a stronger curvature towards the ZB. Also, the \(\Delta_1(02)\) mode shows a positive slope here in contrast to CaF2, where it is negative.

In summary, the Grüneisen parameters span a comparable range in both substances. The wave vector dependence of the parameters for the Δ and Λ direction shows a weaker curvature than in CaF2, especially in the vicinity of the ZB.

From shell-model calculations, Ruppin[67] obtained a very similar mode-Grüneisen dispersion; only the labels \(O1 \leftrightarrow O2\) have been interchanged.

4. Mode-Grüneisen parameters: LO, TO, and Raman modes

Experimental mode-Grüneisen parameters for TO and LO modes seem to be rare, while Raman data are somewhat more abundant. Available theoretical and experimental data of the mode-Grüneisen parameters of the optical Γ modes are collected in Table V.

<table>
<thead>
<tr>
<th>Method</th>
<th>TO</th>
<th>LO</th>
<th>Raman</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABINIT</td>
<td>2.64</td>
<td>1.23</td>
<td>1.99</td>
<td>Present</td>
</tr>
<tr>
<td>Shell model</td>
<td>2.31</td>
<td>0.81</td>
<td>2.03</td>
<td>67</td>
</tr>
<tr>
<td>Mott-Littleton</td>
<td>2.67</td>
<td></td>
<td></td>
<td>68</td>
</tr>
<tr>
<td>Model</td>
<td>2.51</td>
<td>1.01</td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>Expt.</td>
<td>2.4</td>
<td></td>
<td>0.8</td>
<td>43</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td>1.8</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td>2.0</td>
<td>72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td>1.78</td>
<td>73</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From temperature dependent data[43] and with the help of the coefficient of linear thermal expansion[56] \(\alpha_T=19.9 \times 10^{-6}\) K\(^{-1}\) at 300 K, we estimate \(\gamma_{\text{TO}}=2.0\) at RT, similar to the value for CaF2, but slightly smaller than our value \(\gamma_{\text{TO}}=2.64\).
The value $\gamma_{\text{Raman}} = 1.36$ derived\textsuperscript{75} from the temperature dependence is much smaller, and our estimate with the use of data from Ref. 76 gives a similar value $\approx 1.5$.

The temperature dependence of the Raman mode is larger in BaF$_2$ than in CaF$_2$, while the pressure dependence of the Raman mode is about the same,\textsuperscript{70} and that of the TO mode is smaller in BaF$_2$ than in CaF$_2$.

5. Mode-Grüneisen parameters: Long-wavelength acoustic modes

The mode-Grüneisen parameters of the long-wavelength acoustic modes have been obtained from the change of the dispersion-curve slopes with the change of volume. Present and experimental results are collected in Table VI.

While the experimental data for the TA[001] mode from ultrasound measurements\textsuperscript{53} at 298 K and from thermal-expansion measurements\textsuperscript{77} agree well, our theoretical value from the dispersion relation deviates rather strongly. A 6 $\times$ 6 $\times$ 6 k-point mesh might improve the agreement. However, the mode-Grüneisen parameters for the TA mode in the [111] direction is clearly positive in our calculation.

6. Pressure dependence of the elastic constants

Because of the linear relation $\omega_q = c_q q$ for the long-wavelength acoustic modes with the sound velocities $c_q$ and since the $c_{ij}$ are proportional to linear combinations $f_q(c_{ij})$ of the elastic constants $c_{ij}$, the mode-Grüneisen parameters can be written as

$$\gamma_q = -\frac{d \ln \omega_q}{d \ln V} = -\frac{1}{2} \frac{d \ln f_q}{d \ln V},$$

characterizing the change of the elastic constants with the change in volume. In particular one has, e.g.,

$$\gamma_{\text{TA}[001]} = -\frac{1}{2} \frac{d \ln c_{44}}{d \ln V}, \quad \gamma_{\text{LA}[001]} = -\frac{1}{2} \frac{d \ln c_{11}}{d \ln V}.$$  

Assuming the relation $B=-(dp)/(d \ln V)$ with the bulk modulus $B=(c_{11}+2c_{12})/3$, the volume dependence of phonon frequencies or elastic constants can be converted into the pressure dependence,

$$\frac{d \ln c_{ij}}{dp} = -\frac{1}{B} \frac{d \ln c_{ij}}{d \ln V}.$$  

These values are shown in Table VII and have been obtained from interpolation of data at the lattice constants $a=5.9, 6.0$ and $a=6.05$ Å. These values have been chosen to show the nonlinearity of the elastic constants under pressure. An analogous nonlinearity can be seen for the $\Gamma$- and $X$-point modes in Fig. 5. Otherwise the data in Tables VI and VII would be related to each other simply by the bulk modulus, see Eq. (2). For consistency we have taken the theoretical bulk modulus $B=89.8$ GPa. With somewhat too small a lattice constant, the force constants and thus elastic constants result in too large values, which amount to a factor of about 1.5 by which the bulk modulus is too large and the pressure dependence is too small. This, together with the deviations found in Sec. V A 5, should be taken into account when comparing the theoretical with the experimental values in Table VII.

The experimental data are in very good agreement, and if our theoretical data are multiplied by a factor of about 1.5 (correcting for the overestimated value of the bulk modulus) they would come much closer to the experimental values. Also, only small difference between theoretical and experimental values is to be expected, since upon cooling from
TABLE VIII. BaF$_2$: calculated and experimental results for the effective charge $Z^*$ and the high-frequency dielectric constant $\varepsilon_\infty$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ [Å]</th>
<th>$Z^*$</th>
<th>$\varepsilon_\infty$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABINIT (HGH)</td>
<td>6.05</td>
<td>2.634</td>
<td>2.472</td>
<td>Present</td>
</tr>
<tr>
<td>ABINIT (HGH)</td>
<td>6.2</td>
<td>2.585</td>
<td>2.398</td>
<td>Present</td>
</tr>
<tr>
<td>ABINIT</td>
<td>6.095</td>
<td>2.61</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>DFT-LCAO</td>
<td>6.32</td>
<td>2.012</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>OLCAO-LDA</td>
<td>6.2</td>
<td>1.12</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>LCAO-LDA (TDDFT)</td>
<td></td>
<td>1.97</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>Wien97</td>
<td>6.233</td>
<td>2.129</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Crystal98</td>
<td>6.35</td>
<td>1.904</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Bond orbital</td>
<td>6.21</td>
<td>2.15</td>
<td></td>
<td>in 80</td>
</tr>
<tr>
<td>Shell model</td>
<td>6.2</td>
<td>1.96</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Model calc.</td>
<td>2.564</td>
<td></td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>IR exp. (300 K)</td>
<td></td>
<td>2.16</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Optical exp.</td>
<td></td>
<td>1.95</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>Expt. (300 K)</td>
<td>2.150</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Expt. (4 K)</td>
<td>2.18</td>
<td></td>
<td></td>
<td>in 42</td>
</tr>
<tr>
<td>Expt. (300 K)</td>
<td>6.184</td>
<td>2.167</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

room to low temperature the pressure derivatives changes only by a few percent with a maximum change by about 10% in $c'$ and $c_{44}$. The pressure derivative $(d \ln c')/(dp)$ is negative, as is $(d \ln c')/(dV)$, from theory and experiment in contrast to the other values. The relatively small modulus of it is also found in CaF$_2$.53

B. Volume dependence of the high-frequency dielectric constant and of the Born effective charges

In ionic crystals like the fluorites one has an LO-TO splitting. In BaF$_2$ at the $\Gamma$ point there is a threefold-degenerate Raman-active mode near 31.25 meV and an infrared-active mode near 24.72 meV, where the LO mode experiences a huge LO-TO splitting given by

$$\omega^2_{\text{LO}} - \omega^2_{\text{TO}} = \frac{\mu}{V_0} \frac{(Z' \varepsilon)^2}{\varepsilon_\infty}.$$

with $\hbar \omega_{\text{LO}} = 43.576$ meV and $\hbar \omega_{\text{TO}} = 24.715$ meV. BaF$_2$ shows a similarly huge but slightly smaller splitting than CaF$_2$ (nearly 30 meV).

The Born effective charges are $Z^* = Z'_{\text{Ba}} = -2Z'_{\text{F}}$. Because of the cubic symmetry of the present system, the tensors of the dielectric constant and of the Born effective charges are diagonal.

The effective charges $Z^*$ and the high-frequency dielectric constant $\varepsilon_\infty$ have been calculated within the method of linear response. Table VIII lists various experimental and theoretical results.

1. Ground-state dielectric constant

The electrons of Ba are more extended and thus more polarizable than those in Ca resulting in a more polarizable system and in a higher dielectric constant. In general the high-frequency dielectric constant is believed to be overestimated by DFT in the LDA and GGA. The reason is seen in the underestimation of the band gap in LDA and GGA (see Sec. III B). Also our LDA calculation overestimates the value for $\varepsilon_\infty$. The agreement with experiment becomes a bit better when the experimental lattice constant $a = 6.2$ Å is used, see Table VIII or Fig. 8 below.

Inclusion of the so-called scissors operator changes the value from $\varepsilon_\infty = 1.12$ to $\varepsilon_\infty = 1.07$ (at $a = 6.2$ Å).28 Ab initio and deformation-shell model calculations result in values between 1.74 and 2.18.82

2. Ground-state effective charges

The effective charge of Ba is $Z^* = 2.634$ at the theoretical ground state volume $V = 374$ a.u. As in CaF$_2$ also in BaF$_2$ the effective charge is larger than the nominal ionic charge $Z_{\text{Ba}} = 2$. With the use of the experimental lattice constant, which is larger than the relaxed one, $Z^*$ results in a somewhat smaller value.

3. Volume dependence

Both the high-frequency dielectric constant $\varepsilon_\infty$ as well as the effective charge $Z^*$ have been calculated within ABINIT for different volumes. The results are shown in Figs. 7 and 8.

At the theoretical equilibrium volume we find $(d \ln Z^*)/(d \ln V) = -0.25$, from pressure experiments43 the value $-0.3$ is derived.

For the volume derivative of the dielectric constant we find $(d \varepsilon_\infty)/(d \ln V) = -1.048$, in good agreement with $-1.07$ from Dutt et al.,69 Sharma and Shanker obtained with electronic polarizabilities (Ruffa theory) a strain derivative of $-1.15$, somewhat larger than in CaF$_2$. A Penn-model calculation gives the wrong sign.68

As already seen in CaF$_2$, the dielectric constant as well as the effective charge shows a nonlinear volume dependence which indicates the importance of processes in perturbation theory beyond lowest order, in contrast to Ref. 24 where a linear dependence on pressure is claimed.
VI. CONCLUSIONS

We have presented a full ab initio study of the ground-state and vibrational properties of BaF$_2$ in generally good agreement with experimental and other theoretical data.

Due to the same crystal structure and due to nearly the same valence-electronic configuration of the Ba and Ca atoms, many findings are qualitatively similar to those encountered in CaF$_2$.

The electronic band structures of the two systems resemble each other. With the atoms in CaF$_2$ closer together than in BaF$_2$ the bands are narrower in the latter material. But there is a qualitative difference: The valence-band maximum of the electronic band structure of BaF$_2$ occurs in the $\Sigma$ direction, while it is at the $X$ point in CaF$_2$.

As in other materials, also the present lattice constant turns out to be smaller than the experimental one in the LDA and larger in the GGA. Consequently, the force constants, elastic constants, and phonon frequencies are somewhat too large in the LDA and too small in the GGA. Because of the mass of the Ba atom being larger than the Ca mass, the phonon frequencies in BaF$_2$ are generally smaller than those of CaF$_2$.

There are clear indications of a nonlinear volume and pressure dependence of all phonon properties. All modes soften upon expansion at a comparable rate (the rate being much smaller for the $X'_4$ and $X'_5$ modes) despite different irreducible representations, and a number of modes go soft at about a 10\% increase of the equilibrium lattice constant. The mode-Grüneisen parameters of the $\Delta_1$, $\Delta_2$, $\Delta_3(O2)$, and $\Lambda_3$ modes behave similarly in BaF$_2$ and CaF$_2$, while there are quantitative and qualitative differences for the (transverse) $\Delta_3(A)$ and $\Delta_4(O1)$ (and longitudinal) $\Lambda_1$ modes.

Upon volume expansion, first the $X_5$ and then the $X'_2$ mode go critically soft in BaF$_2$, while the order is reversed in CaF$_2$. Actually, the first mode to go soft is near the $K$ point. The Born effective charge $Z' = 2.6$ of the Ba$^{2+}$ ion is larger than the nominal ionic charge and even larger than that in CaF$_2$ ($Z' = 2.4$).

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VOLUME AND PRESSURE DEPENDENCE OF GROUND-STATE PROPERTIES OF DENSITIES OF MATTER — XI. APPROXIMATE EQUATIONS OF STATE OF DENSE HE, HD, AND TIDAL STABILITY OF HEDGES


S. S. Mitra (unpublished), cited in Ref. 70.


