

## *Ab initio* study of piezoelectricity and spontaneous polarization in ZnO

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We demonstrate the feasibility of *ab initio* studies of piezoelectricity within an all-electron scheme. The focus of our analysis is on wurtzite ZnO; for comparison, some results are also presented for the related materials BeO and ZnS. The comparative study is performed in order to understand the microscopic origin of the peculiar behavior of ZnO, whose piezoelectric response is the strongest among the tetrahedrally bonded semiconductors. In all such materials, the piezoelectric effect results from two different terms of opposite sign: these are usually referred to as the “clamped-ion” and the “internal-strain” contributions. Cancellation amongst them is least effective in ZnO, where the dominant effect is due to a rigid-ion-like mechanism. Furthermore, we compute the spontaneous polarization of ZnO and we discuss the puzzling agreement between our calculated value and a very indirect experimental estimate of the same quantity.

### I. INTRODUCTION

Among the tetrahedrally bonded semiconductors, ZnO has the highest piezoelectric tensor.<sup>1</sup> This property makes it a technologically important material in many practical applications which require a large electromechanical coupling.<sup>2</sup> For this reason ZnO has been studied extensively from an experimental point of view and by now its mechanical and electrical properties are very well known.<sup>3</sup> However, the reasons for this unusual piezoelectric behavior are unclear. By comparing ZnO with similar II-VI compounds such as ZnS, CdS, and CdSe, which share the same wurtzite structure, it is found that the piezoelectric tensor of the other materials are at most one-half of the ZnO compound. Furthermore, a compound such as BeO, which has the same structure and the same anion, has one of the smallest piezoelectric tensors among the II-VI and III-V semiconductors, an order of magnitude smaller than in the case of ZnO.

In this work we demonstrate that an *ab initio* study of the piezoelectric effect in ZnO is feasible, and accurately predictive. Another aim of the present work is showing how to deal with piezoelectricity when the major simplifications of a pseudopotential scheme cannot be exploited. Our main result is a clear identification of the origin of the strong piezoelectric effect in ZnO. Some limited additional calculations, performed on BeO, which is isoanionic, and ZnS, which is isocationic, allow further insight into the phenomenon.

This paper relies on several theoretical advances which by now allow a completely *ab initio* study of the piezoelectric properties of ZnO. The first important step has been the demonstration of the bulk nature of the piezoelectric effect. In a fundamental paper,<sup>4</sup> Martin showed that the piezoelectric tensor is a bulk property of a solid, independent from surface effects, and that it can in principle be computed from the electronic wave functions. More recently it has been shown that the Kohn-Sham orbitals, obtained in the framework of density-functional

theory,<sup>5</sup> are accurate enough to yield meaningful predictions for the piezoelectric tensors both in III-V (Ref. 6) and II-VI (Refs. 7 and 8) semiconductors. In these calculations, the piezoelectric tensor was evaluated as the stress linearly induced by a macroscopic electric field. Technically, the computations relied on linear-response theory combined with a plane-wave expansion of the wave functions, in a pseudopotential scheme. The same methods do not suffice to study the properties of a “difficult” material such as ZnO. The use of a plane-wave expansion is neither suited to describe localized orbitals such as the zinc *d* ones nor is it efficient for dealing with a first-row element such as oxygen. In materials such as ZnSe or ZnTe it is possible to approximately account for the *d* electrons by including them in the frozen core.<sup>9</sup> On the contrary, it is well known<sup>10,11</sup> that in ZnO the zinc *d* electrons strongly hybridize with the oxygen *p* ones, thus giving important contributions both to the bonding properties of the material and to its electrical response. These *d* electrons are very localized around the nuclei: this feature, together with the presence of oxygen, would require a plane-wave basis set of prohibitive size. In this material, a much more convenient scheme for electronic-structure calculation is provided by the full-potential linearized augmented-plane-wave (FLAPW) method.<sup>12</sup>

Finally, the latest theoretical advance exploited in the present work is the modern theory of macroscopic polarization, due to King-Smith and Vanderbilt<sup>13</sup> (for an alternative derivation and a review see also Ref. 14). Instead of computing the stress linearly induced by an electric field, we compute here the polarization linearly induced by macroscopic strain. This quantity is efficiently evaluated—within any basis set—from the overlap between Bloch wave functions computed on neighboring **k** points. The accuracy of this alternative approach was tested with respect to linear-response calculations in the original paper and in some subsequent applications,<sup>8</sup> and the equivalence of the two techniques is now completely established even from a numerical viewpoint, when plane

waves are used.

In a wurtzite structure the homogeneous macroscopic strain is in general coupled to an internal *microscopic* strain, i.e., to a relative displacement of the cationic and anionic sublattices. In the Born-Oppenheimer approximation, the macroscopic piezoelectric tensor results from two distinct contributions: a purely electronic one, called hereafter clamped-ion term, and evaluated at vanishing microscopic strain and one due to the relative displacement of the sublattices, which is equivalent to a zone-center optic phonon. There is no easy experimental access to each of the two terms separately. The available calculations for zinc-blende-structure semiconductors invariably found these two terms of similar magnitude and of opposite sign, the actual value of the piezoelectric tensor resulting then from a strong cancellation between them.

The main finding of this work is that in ZnO the clamped-ion contribution to the piezoelectric polarization is about half (in modulus) the final value, such that the cancellation is much less effective, and internal strain is responsible for the dominant term. The same behavior is found for BeO as well. However, the actual value of the internal-strain relaxation is much smaller in BeO than in ZnO, thus accounting for the different piezoelectric properties of the two oxides. The isocationic wurtzite ZnS behaves instead more like the zinc-blende-structure materials, where the two terms undergo a significant cancellation. Incidentally, a pseudopotential study of ZnS in the metastable zinc-blende structure was previously performed<sup>7</sup> and some useful comparisons with the present results are possible. Finally, we observe that no important role seems to be played by the Born effective charge, whose absolute value is close to the nominal ionicity (i.e., 2) in all the II-VI's compounds studied so far.

The spontaneous polarization is a by-product of the present calculation. Though this quantity has never been measured, our value is in embarrassing agreement with the existing very indirect estimate of the same quantity. The reasons why this agreement appears so surprising are discussed, and an intriguing issue is left open.

This paper is organized as follows. In Sec. II we review the main definitions which are necessary to deal with the piezoelectric tensor in a wurtzite structure. In Sec. III we give the technical details of the electronic-structure calculations presenting the FLAPW band energies and charge densities<sup>15</sup> of ZnO, together with those of ZnS and BeO. In Sec. IV we present our computation of the piezoelectric tensor of ZnO and we discuss the results in connection with analogous calculations performed on the reference materials BeO and ZnS. Section V is devoted to the issue of spontaneous polarization. Section VI contains our conclusions.

## II. PIEZOELECTRICITY IN WURTZITE-STRUCTURE CRYSTALS

ZnO is a tetrahedrally coordinated semiconductor with wurtzite structure. This structure has a hexagonal Bra-

vais lattice with four atoms per unit cell.<sup>16</sup> It is completely defined by the length of the hexagonal edge  $a_0$ , the height  $c_0$  of the prism, and a microscopic dimensionless parameter  $u$ , which is defined as the length of the bond parallel to the  $c$  axis, in units of  $c$ . The piezoelectric tensor has three independent components ( $C_{6v}$  point group).<sup>17</sup> Two of these components measure the polarization induced along the  $c$  axis, at zero electric field, by a uniform strain either along the  $c$  axis or in the basal plane. The relevant relationship, in Voigt notation, is

$$P_3 = e_{33}\epsilon_3 + e_{31}(\epsilon_1 + \epsilon_2), \quad (1)$$

where  $\epsilon_3 = (c - c_0)/c_0$  is the strain along the  $c$  axis,  $\epsilon_{1,2} = (a - a_0)/a_0$  is the strain in the basal plane, and  $e_{33}, e_{31}$  are the piezoelectric coefficients. The third independent component of the piezoelectric tensor describes the polarization induced perpendicularly to the  $c$  axis by a shear strain and will not be considered in this work. The sign of the piezoelectric tensor is fixed assuming that the positive direction along the  $c$  axis goes from the cation to the anion.

Equation (1) is a macroscopic phenomenological equation which is valid in the linear regime for small strain values. It defines the piezoelectric tensor through the change in polarization induced by variations of the cell parameters  $a$  and  $c$  only. From a microscopic point of view, and within the Born-Oppenheimer approximation, a strain parallel or perpendicular to the  $c$  axis produces also an internal displacement of the zinc sublattices with respect to the oxygen ones, i.e., a variation of the parameter  $u$  of the wurtzite structure.<sup>16</sup> The measured polarization is due both to the effect of the change of the macroscopic cell parameters *and* to the associated change of  $u$ , as we anticipated in the Introduction. We therefore separate, in analogy with the zinc-blende case, a clamped-ion term and a term due to internal relaxation:

$$e_{33} = e_{33}^{(0)} + \left. \frac{\partial P_3}{\partial u} \right|_{\epsilon_3} \frac{du}{d\epsilon_3}, \quad (2)$$

where

$$e_{33}^{(0)} = \left. \frac{\partial P_3}{\partial \epsilon_3} \right|_u, \quad (3)$$

and analogous relationships hold for  $e_{31}$ .

We analyze for the time being only the  $e_{33}$  coefficient, thus keeping  $a$  fixed to its equilibrium value  $a_0$ . The change of polarization linearly induced by a relative sublattice displacement (variation of  $u$ ) can be measured by an effective charge  $Z^*$ .<sup>18</sup>

$$\left. \frac{\partial P_3}{\partial u} \right|_{\epsilon_3} = \frac{4e}{\sqrt{3}a_0^2} Z^*, \quad (4)$$

where  $e$  is the electron charge. In order to compare the different contributions and different materials it proves useful to refer to dimensionless quantities. Defining  $\bar{e}_{33} = 2a_0^2 e_{33}/e\sqrt{3}$  we have

$$\bar{e}_{33} = \bar{e}_{33}^{(0)} + \frac{8}{3} Z^* \frac{du}{d\epsilon_3}. \quad (5)$$

Equation (3) shows that we can obtain the clamped-ion piezoelectric tensor from the slope of the straight line yielding polarization versus strain at fixed  $u$ . Eventually, the total piezoelectric tensor is recovered by evaluating the effective charge from the derivative of the polarization with respect to  $u$  at fixed  $c$  and from the knowledge of the  $u$  variation induced by macroscopic strain. This latter derivative can be evaluated from simple energetic considerations, knowing the equilibrium value of  $u$  as a function of the structural parameter  $c$ . The two other quantities require instead the computation of the polarization variation induced by a change of either  $c$  or  $u$ .

The variation of the polarization can be obtained using a method introduced recently by King-Smith and Vanderbilt<sup>13,14</sup> which allows one to compute the *difference* in polarization between any two states of the same crystal, under the hypothesis that these two states can be transformed into each other by the adiabatic variation of a suitable parameter in the crystal Hamiltonian. An additional necessary condition is that the solid remains an insulator throughout the transformation. The key point of the method is the evaluation of a geometric quantum phase:<sup>19</sup> its main ingredients are the phases  $\varphi(\mathbf{k}, \mathbf{k}')$ , defined as the phases of the overlap-matrix determinants

$$S_{mn}(\mathbf{k}, \mathbf{k}') = \langle \chi_m(\mathbf{k}) | \chi_n(\mathbf{k}') \rangle, \quad (6)$$

where  $\chi_n(\mathbf{k}')$  is the periodic part of the valence Bloch wave functions. The difference in electronic polarization can be obtained from these phases by an integration over a unit cell of the reciprocal lattice.

Let us call  $\lambda$  a parameter of the crystal Hamiltonian, which in our case could be either  $c$  or  $u$ : the electronic term in the polarization difference is then:<sup>13</sup>

$$P(\lambda) - P(\lambda=0) = -\frac{2e}{(2\pi)^3} \left[ \int d\mathbf{k} \frac{\partial}{\partial k'_3} \varphi_\lambda(\mathbf{k}, \mathbf{k}') \Big|_{\mathbf{k}'=\mathbf{k}} - \int d\mathbf{k} \frac{\partial}{\partial k'_3} \varphi_{\lambda=0}(\mathbf{k}, \mathbf{k}') \Big|_{\mathbf{k}'=\mathbf{k}} \right], \quad (7)$$

where the two integration domains are reciprocal unit cells of the solids characterized respectively by a finite  $\lambda$  or by  $\lambda = 0$ . When  $\lambda$  is identified with  $u$  the two domains coincide; when  $\lambda$  is identified with  $c$  they can be trivially made to coincide upon scaling.<sup>14</sup> In practice, the wave functions are evaluated on a discrete mesh. In the basal plane we use an irreducible set of three  $\mathbf{k}$  points. Along the reciprocal  $c$  axis, we use a discrete mesh of 20  $\mathbf{k}$  points. We calculate the wave functions in these 60 points after having performed a self-consistent calculation with six special  $\mathbf{k}$  points.

### III. FLAPW CALCULATIONS

All our calculations are performed within the self-consistent FLAPW method.<sup>12</sup> The local-density approximation (LDA) to the density-functional theory with the Hedin-Lundqvist exchange and correlation potential has been used. In all our calculations we chose equal atomic-sphere radii for anions and cations: their values are 1.8 a.u. in ZnO and ZnS and 1.5 a.u. in BeO. In the inter-

stitial region the wave functions include all plane waves with energies up to 4.35 Ry in ZnO and ZnS and less than 4.2 Ry in BeO. Inside the spheres the wave functions are expanded in products of radial functions and spherical harmonics with principal angular momentum  $l \leq 8$ . The crystal charge and potential are expanded in an analogous basis set with wave vectors whose modulus is less than 9.5 a.u. in ZnO and ZnS and 10 a.u. in BeO. The core states are calculated fully relativistically and updated at each iteration, whereas the valence states (O 2s, O 2p, S 3s, S 3p, Be 2s, Zn 3d, and Zn 4s) are treated semirelativistically. The overlap matrices Eq. (6) are evaluated<sup>20</sup> in the FLAPW representation.

In order to determine the set of lattice parameters which minimize the total energy in ZnO and BeO we proceed in two steps. We first fix  $c/a = \sqrt{8/3}$  and  $u = 3/8$ , which are the “ideal” values, ensuring perfect tetrahedral coordination. We then vary  $a$  to determine the volume which minimizes the total energy. We found  $\Omega_0 = 45.89 \text{ \AA}^3$  for ZnO and  $\Omega_0 = 26.64 \text{ \AA}^3$  for BeO. These volumes are considered as the equilibrium LDA volumes. Then, in order to determine the parameters  $c/a$  and  $u$ , we computed the total energy at several points of the  $(u, c/a)$  plane, at fixed volume. The total-energy surface around the minimum is described by a parabolic function with 6 parameters which are determined by a least-square fit over 14 configurations. The rms errors turn out to be 0.07 mRy in ZnO and 0.03 mRy in BeO; however, since a few points have a much larger error we assume for both compounds—as a safe estimate—an error of 0.5 mRy on the total energies. In Fig. 1 we show the results for both ZnO and BeO on the same energy scale. Experimentally it is well known that BeO is much harder than ZnO and in fact in BeO the 0.5 mRy curve encircles a small region of the  $(u, c/a)$  space. The position of the minimum inside this region is in good agreement with the experimental data. On the contrary in ZnO the 0.5 mRy curve does not define a sufficiently small region of the parameters space. Both the experimental point and the theoretical point are, however, within this region. Since—on the

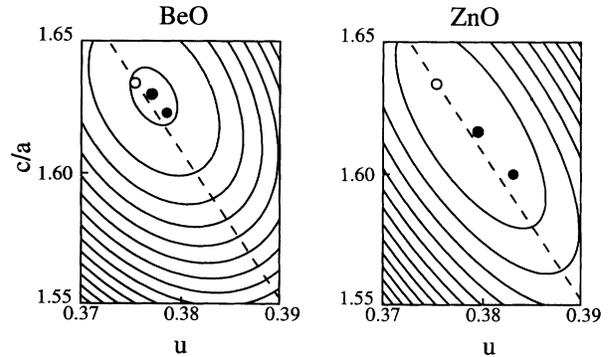


FIG. 1. Theoretical constant energy contours in the  $(u, c/a)$  plane for hexagonal BeO and ZnO at constant unit cell volume  $\Omega_0$ . The spacing between contours is 0.5 mRy. The solid circles indicate, respectively, the ideal (white), the theoretical (gray), and the experimental (black) configurations. The dashed line corresponds to structures with equal bond lengths.

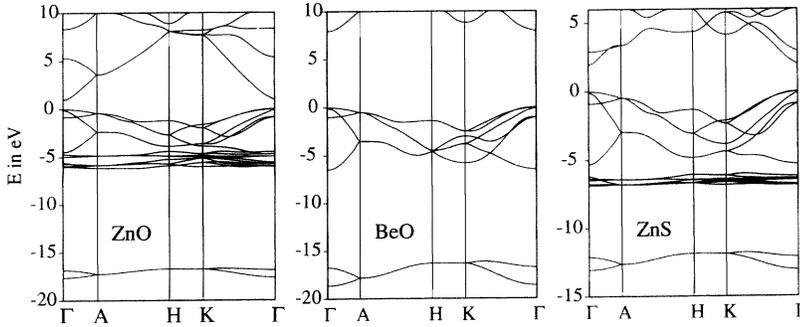


FIG. 2. Energy bands of hexagonal ZnO, BeO, and ZnS along the main symmetry lines of the Brillouin zone.

basis of experimental data—we expect a large value for the piezoelectric tensor of ZnO, this problem of the exact determination of the LDA equilibrium structure of ZnO does not constitute a real limit. We have thus chosen the unstrained equilibrium structure as follows: for BeO the theoretical LDA minimum  $a = 5.042$  a.u.,  $c/a = 1.629$ ; for the other materials the experimental values  $a = 6.147$  a.u.,  $c/a = 1.602$  (ZnO) and  $a = 7.222$  a.u.,  $c/a = 1.638$  (ZnS). As for the  $u$ 's, the numerical error is much smaller and the theoretical values agree pretty well with the experiment.

At these values of the parameters we have computed the energy bands of the three compounds. In Fig. 2 we show the results. The LDA bands of ZnO and ZnS have been computed earlier<sup>10</sup> using a pseudopotential scheme and a localized-orbital basis set. The agreement with the present results is quite good. It is well known that the eigenvalues of the Kohn-Sham equation must *not* be identified with the single-particle excitation energies. Notwithstanding, it has become a common practice to compare the energy bands with photoemission data and usually the agreement for the  $sp$  bands is found to be satisfactory in many materials. As noted in Ref. 10, this

is the case also for ZnO and ZnS, but the position of  $d$  bands is not in agreement with photoemission data, which predict narrow states around  $-8$  eV. Our calculation in fact agrees with the previous LDA one,<sup>10</sup> and we find the  $d$  bands at least 4 eV higher than the photoemission experiments. We cannot assess whether this must be ascribed to density-functional theory, to LDA, or to both; we just mention that a recent Hartree-Fock calculation<sup>11</sup> predicts instead the  $d$  bands about 2 eV too low.

The total valence charge densities of ZnO and BeO are displayed in Fig. 3. This figure shows that both ZnO and BeO look like strongly ionic materials, despite the amount of  $pd$  hybridization which is present<sup>10,11</sup> in ZnO and obviously not in BeO. The ionic radius of beryllium appears much smaller than the one of zinc and this feature could in part explain the different mechanical behavior of the two materials as we will discuss below.

#### IV. INDUCED POLARIZATION IN ZINC OXIDE

We will discuss mainly the computation of  $e_{33}$ , since the computation of  $e_{31}$  is completely equivalent. In Fig. 4 we plot the values of the polarization versus  $\epsilon_3$ , obtained

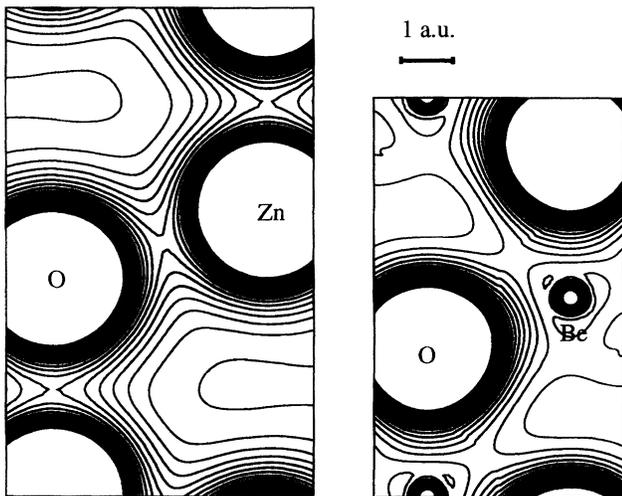


FIG. 3. Valence charge density plots of ZnO and BeO projected on the plane parallel to the  $c$  axis which contains both anions and cations. Subsequent contours differ by 0.01 a.u.

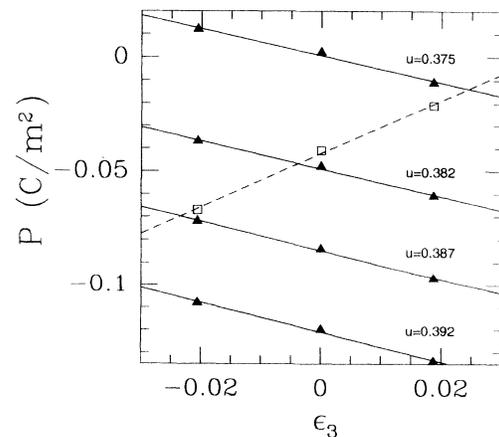


FIG. 4. Polarization of ZnO versus  $\epsilon_3$  for several values of  $u$  (filled triangles) and at the equilibrium values of  $u$  for a given  $\epsilon_3$  (empty squares). The slope of the solid lines gives  $e_{33}^{(0)}$ , while the slope of the dashed line gives the total piezoelectric tensor.

using Eq. (3) and calculated for several values of  $u$  (filled triangles; the open squares will be discussed below). It can be seen that for a given  $u$  value, the polarization is a linear function of  $\epsilon_3$  in this range (solid lines) and, furthermore, that the  $\epsilon_3$  derivative is independent of  $u$ . This derivative is fairly small, yielding the clamped-ion piezoelectric coefficient reported in Table I: this is opposite in sign to the total measured effect and about one-half of its modulus.

The opposite sign of the two contributions is typical of all the tetrahedrally bonded materials either having zinc-blende structure, previously studied using pseudopotentials,<sup>6-8</sup> or having wurtzite structure, studied here. In III-V materials the clamped-ion term is usually larger than the contribution due to the internal strain, resulting in a negative value of the piezoelectric coefficient, while in II-VI materials the opposite happens and the sign becomes positive. However, the absolute value of each of the terms is usually much larger than the final value, resulting from a large cancellation: therefore ZnO is unusual in this respect, since we have only a 50% cancellation. It is worth mentioning that in a rigid ion model the clamped-ion part is exactly zero. For a comparison, we also report in Table I the value of the clamped-ion piezoelectric tensor for the two reference materials. When comparing the relative importance of the two terms, BeO is as atypical as ZnO while ZnS is a more typical case.

To proceed further, and according to the above equations, we need the derivative of  $u$  with respect to the strain and the effective charge of one of the two types of atoms. The effective charge is obtained again from Eq. (7) by computing the polarization of the solid for several values of the parameter  $u$ , with  $a$  and  $c$  fixed at their unstrained value. The  $Z^*$  obtained for the three materials are reported in Table I: they refer to the effective charge of the anion, which in our coordinate system is the atom which moves when  $u$  is changed. The values are in agreement with the experimental data reported in Ref. 4.

The computation of the derivative  $du/d\epsilon_3$  is the most difficult part of the calculation. It is equivalent to the computation of the internal strain parameter of the zinc-blende structure, which has been shown to be very sensitive to the lattice constant both in GaAs (Ref. 6) and in CdTe,<sup>8</sup> and for this reason our evaluation of this parameter is the quantity which in ZnO and ZnS is mostly affected by the use of the experimental structure. The experimental measurement of this quantity is not very pre-

cise either and the values obtained from indirect derivations<sup>21</sup> usually are too rough to yield meaningful estimates of the piezoelectric constant, particularly in systems with wurtzite structure.<sup>4</sup> We have used strain values up to  $\pm 2\%$  and we have computed the equilibrium  $u$  for several values of the strain. The equilibrium  $u$  has been obtained by fitting with a fourth-order polynomial the total energy computed for seven different values of  $u$ .

In Fig. 5 we display for ZnO the values of  $u$  at fixed  $a$  as a function of the strain  $\epsilon_3$ . For comparison we report also the computed dependence of  $u$  upon the strain in the cases of BeO and ZnS. From the slope of these curves we obtained the values of  $du/d\epsilon_3$  reported in Table I. This figure shows that  $du/d\epsilon_3$  in ZnO is similar to all the other tetrahedrally bonded semiconductors, while in this respect BeO has an extremely anomalous behavior. A quantitative explanation of this low value of  $du/d\epsilon_3$  in BeO requires further studies, but a qualitative explanation could be found in the extremely small size of the beryllium ions (see Fig. 3), which, due also to the lack of  $d$  electrons, favors under strain the bond-length relaxation with respect to the bond-angle one. This interpretation is supported by a comparative study of macroscopic elasticity in all the tetrahedral compounds, performed many years ago by Martin,<sup>22</sup> and where BeO behaves in a qualitatively different way from the other materials.

From the knowledge of the polarization induced by a variation of  $c$  and by a corresponding variation of  $u$  we can compute, using Eq. (2), the total change of polarization due to a macroscopic strain. In Fig. 4 we report our results for several values of  $\epsilon_3$  (empty squares). These values have been interpolated by a straight dashed line around  $\epsilon_3 = 0$ . From the slope of the curve we get  $\bar{e}_{33} = 0.92$ , which is within the range of experimental data. The other theoretical values of  $\bar{e}_{33}$  for BeO and ZnS are also reported in Table I. While the agreement between theory and experiment is very good for ZnS, in the case of BeO we find a large disagreement. We point out, however, that the piezoelectric tensor of BeO is very small and its experimental measurement<sup>1</sup> is quite old; we were not able to find more recent data. At this point this disagreement is an open issue of the present approach: we have checked that it does not appreciably depend on the equilibrium geometry used in the calculations. We simply note that trusting the theoretical value of  $\bar{e}_{33}^{(0)}$ , the value of  $du/d\epsilon_3$  compatible with the experimental  $\bar{e}_{33}$  would be  $-0.04$ , one-half of our result, and this would mean a highly anomalous mechanical behavior of BeO with respect to the other tetrahedrally bonded

TABLE I. Computed and experimental values of the  $\bar{e}_{33}$  component of the piezoelectric tensor of ZnO, BeO, and ZnS and of its decomposition in a clamped-ion and ionic contributions. The computed and experimental effective charges for each compound are also shown.

	$\bar{e}_{33}^{(0)}$	$Z_O^*$ (Theor.)	$Z_O^*$ (Expt. <sup>a</sup> )	$du/d\epsilon_3$	$\bar{e}_{33}$ (Theor.)	$\bar{e}_{33}$ (Expt. <sup>b</sup> )
ZnO	-0.44	-2.05	-2.10	-0.25	0.92	0.76 - 1.18
BeO	-0.15	-1.72	-1.85	-0.09	0.26	0.05
ZnS	-0.76	-1.99	-2.00	-0.19	0.24	0.27

<sup>a</sup>Reference 4.

<sup>b</sup>Reference 1.

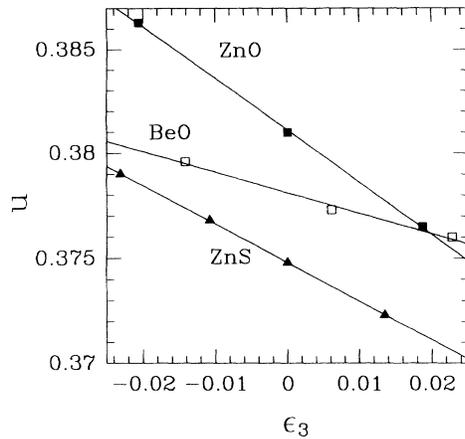


FIG. 5. Values of  $u$  as a function of macroscopic strain  $\epsilon_3$  for ZnO (filled squares), BeO (empty squares), and ZnS (filled triangles). The slopes of the solid lines provide the values of  $du/d\epsilon_3$ .

semiconductors.

The above analysis shows that the large piezoelectric tensor of ZnO with respect to the values found in other materials having the zinc-blende structure is due to the fact that the internal strain is mostly responsible for the effect. In this respect BeO has a similar behavior and this seems to be a characteristic of oxide materials with small cell volumes and ionic character.

Computations similar to those reported above have been performed in order to compute  $e_{31}$  in ZnO. In this case we find that  $du/d\epsilon_1 = 0.24$  and  $\bar{e}_{31}^{(0)} = 0.28$ . From these results, using the same effective charge of oxygen we have  $\bar{e}_{31} = -0.39$ , which is within the range of the reported experimental values, i.e.,  $-0.47 < \bar{e}_{31} < -0.22$ .

An interesting question to raise at this point is the following: how “tetrahedral” are the piezoelectric properties of this material? The piezoelectric tensor has only one independent component in the zinc-blende structure and one expects therefore an approximate relationship between  $e_{33}$  and  $e_{31}$  to hold in our material. Assuming noninteracting tetrahedral units,<sup>23</sup> one guesses  $e_{33} = -2e_{31}$ . This relationship is in fact satisfied to a rather good approximation, despite the fact that ZnO has a very distorted structure with respect to the ideal wurtzite one.

## V. SPONTANEOUS POLARIZATION OF ZINC OXIDE

Last but not least, we briefly discuss spontaneous polarization, which is in fact a by-product of the present calculation. From Fig. 4 its value is clearly  $-0.05$  C/m<sup>2</sup>, about the same as that previously found for BeO.<sup>18,24</sup> Given the strong piezoelectricity of ZnO, the theoretical value is rather sensitive to the structural data used in the calculation.

Spontaneous polarization in a nonferroelectric material has never been directly measured, while one invariably

measures polarization derivatives. One obvious example is the piezoelectric tensor, calculated and compared to experiment throughout this work. As for the “absolute” polarization of a given material, there is some debate whether it is a property which can be defined at all as a *bulk property*, independent of sample termination.<sup>14,25</sup> Our favorite viewpoint has been to conventionally define the spontaneous polarization of a low-symmetry crystal as the polarization *difference* with respect to a high-symmetry structure of the same material. In the case of wurtzite structure our reference choice is the zinc-blende structure, as explained in Ref. 18, and this choice leads to the value reported above for the spontaneous polarization of ZnO. This choice is unique upon symmetry grounds, but it must be agreed that it is a theoretical assumption, bearing no relationship to a real experiment: the only observed bulk quantities are in fact polarization *differences*. In our viewpoint, an identical statement applies even to ferroelectric materials, although in this case the reference structure exists in nature.

It is therefore quite surprising—in view of the present theoretical understanding<sup>14</sup>—that some experimental estimates of the spontaneous polarization in BeO and ZnO do indeed exist.<sup>26</sup> Even more surprising, the estimated absolute values are in embarrassing agreement with our calculations, both for BeO and ZnO, where this figure is in fact  $0.07 \pm 0.02$  C/m<sup>2</sup>. We therefore briefly discuss the idea upon which these estimates are based.

The quantities that have been measured are optic constants and the estimated absolute value of the spontaneous polarization is extracted from the ratio between suitable nonlinear and linear constants. The underlying theory is based on the Landau expansion of the free energy for ferroelectrics, in terms of which the relationship between spontaneous polarization and nonlinear optic constants is almost trivial.<sup>27</sup> The Landau expansion is known to describe pretty well the behavior of many ferroelectrics. Furthermore, in ferroelectrics one can *independently* measure the spontaneous polarization (via polarization reversal) and the nonlinear optic constants: it is found that the relationship between the two kind of measurements agrees well with the predictions of Landau theory. The embarrassing point is that wurtzite-structure materials are not ferroelectric, their polarization is not reversible, and no kind of Landau expansion is meaningfully devisable. However, if one naively applies in this case the same relationship as for ferroelectrics, one finds very good agreement between the experimental estimate and our theoretical result. We do not have any explanation for this agreement and in fact we remain with an open question on this issue. Spontaneous polarization is a nontrivial phenomenon whose real nature has been unveiled only very recently.<sup>13,14,25</sup> According to the present understanding and to our calculations, the spontaneous polarization is a Berry phase of the electronic ground state. It is at present unclear which relationship (if any) might link nonlinear optics to such a geometric quantum phase.

## VI. CONCLUSIONS

We have shown that using modern *ab initio* techniques it is now possible to predict the value of the piezoelec-

tric tensor in a computationally delicate material such as ZnO. We have shown that its large piezoelectric tensor is due to the low value of its clamped-ion contribution. This characteristic is shared also by BeO and seems to be typical of oxide materials, which have a ionic bond and a small unit cell. By comparison with ZnS, which has characteristics more similar to other previously studied II-VI zinc-blende compounds, we have demonstrated that the piezoelectric behavior of ZnO and BeO is very unusual among the tetrahedrally bonded semiconductors. In both these compounds the piezoelectric tensor is dominated by the internal relaxation of anion and cation sublattices induced by the macroscopic strain. Besides this similarity, ZnO is different from BeO in that under strain

the former has a stronger tendency to conserve the bond lengths. Finally, we have discussed the calculated spontaneous polarization and the puzzling agreement between a very indirect—as a matter of fact arbitrary—estimate of the same quantity and our result.

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