Ab Initio Study of the Spontaneous Polarization of Pyroelectric BeO

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The spontaneous bulk polarization of wurtzite BeO is studied using ground-state first-principles theory. This quantity, which is *not* accessible when imposing periodic boundary conditions, is obtained with a novel approach based on the supercell method. The calculated macroscopic polarization is $P_3 = 1.5\times10^{-2}$ C/m^2, and mostly results from the internal crystallographic distortion. No experimental value of P_3 exists, but the calculated *differences* in polarization, between different geometries, compare well with available data.

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The macroscopic polarization of a piece of matter is an essential ingredient in classical electrostatics.[1] In standard quantum-mechanical treatments of real solids, the electronic term of the polarization cannot be obtained, since Born-von-Kármań boundary conditions are used in practice to recover the thermodynamic limit. So far only the polarization *induced* in nonmetals by some perturbation has been investigated in a nonphenomenological way. More specifically, during the past years there has been much work on the dielectric constant[2] (i.e., response to a macroscopic field), while the problem of effective charges in lattice dynamics[3] (i.e., polarization induced by zone-center modes in polar crystals), and that of the piezoelectric constants[4,5] (i.e., polarization induced by strain), have only received limited attention.

The present work deals with the *spontaneous* macroscopic polarization of a crystal. For several low-symmetry classes of crystals, group theory does allow a nonvanishing macroscopic *bulk* polarization (i.e., dipole per unit volume); but in a real, finite sample, this polarization is generally neutralized by electrically active defects and/or surface charges.[1] Bulk polarization can be experimentally detected only in nonequilibrium conditions, when its *variation* is accessible: this is the case of ferroelectricity and pyroelectricity.[1] The latter effect is a very indirect manifestation of spontaneous polarization: The measured pyroelectric constants are only phenomenological in nature, and do not allow us to extract quantitative information[6] about the value of the macroscopic polarization.

We decided to study the spontaneous polarization in BeO, which is—from a theoretical viewpoint—the simplest pyroelectric material: It has the wurtzite (*W*) structure[7,8] (i.e., the highest symmetry compatible with this effect) and its constituents are first-row elements. Previous theoretical studies of this material[9] were performed using the usual periodic boundary conditions, and therefore do not provide any information about macroscopic polarization. We deal with this problem in the framework of state-of-the-art first-principles theory of electronic properties.[10,11] To the best of our knowledge no work—based on quantum mechanics whatsoever—has previously appeared in the literature on this subject.

The quantity we are interested in cannot be obtained from the bulk charge density of the infinite solid, simply because the macroscopic polarization of a charge density distributed all over space is ill defined.[12] We study instead the bulk polarization of a slab of finite thickness, with faces normal to the *c* axis. In order to get rid of surface and truncation effects, we embed the slab in an *ad hoc* medium which (i) has no bulk spontaneous polarization (because of symmetry); (ii) does not produce any chemical (e.g., broken bonds, ionic charge transfer) or geometrical (e.g., reconstruction) perturbation at the interface. The optimal choice for this medium is obviously BeO in the zinc-blende (ZB) structure, grown along (111) at the cubic lattice constant which provides perfect interface matching.

Furthermore, it is convenient to replicate this *W*/ZB interface, and to shortcircuit the end faces. The computational system becomes accordingly a superlattice of fourteen atoms per unit cell, schematically shown in the upper panel of Fig. 1, which can be handled using the standard boundary conditions for an infinite system. Similar supercells have been considered previously in the literature.[13] The interface between the two phases is not unambiguously defined,[14,15] since one material merges continuously into the other. However, for the structure of Fig. 1, where the *W* slab has ideal geometry,[7] the locations of the *conventional* interfaces can be defined on the basis of simple arguments:[13] These interfaces are indicated by vertical broken lines, across Be-O transverse bonds.

We can imagine the construction of our superlattice from an infinite cubic ZB crystal, and generating the *W*

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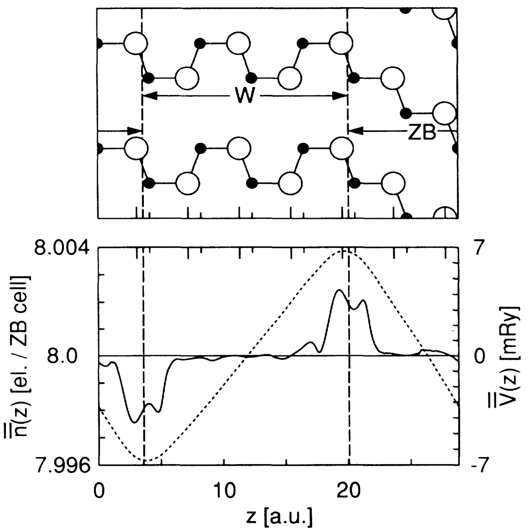

FIG. 1. Upper panel: Stacking diagram of the computational supercell in a vertical plane through Be-O bonds. Solid and open circles represent Be and O atoms, respectively. With the usual conventions for the *W* structure (Refs. 8 and 16), the positive *c*-axis direction points towards the right. Vertical broken lines indicate the conventional interfaces as defined in the text for the ideal *W* slab. Lower panel: Macroscopic averages of the valence electron density (solid line) and of the electrostatic potential energy (dashed line) in the BeO supercell (ideal *W* case).

layers step by step with a suitable sequence of stacking faults. At the end of this process we can measure the polarization *difference* between the final and initial situations. The advantage of our superlattice is that the initial material has, by symmetry, zero bulk polarization: Because of this we have access to the value of the bulk spontaneous polarization of the *W* phase. We notice that also a real finite slab of *W* BeO in vacuum has, in principle, a nonvanishing dipole; however, this dipole depends on truncation, which in turn depends on preferred cleavage.[8,16] We stress that such a dipole—at variance with the one calculated here—is *not* a bulk effect, since it is nonzero even in slabs of cubic materials.

All our calculations are performed within the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method.[11] The local-density approximation (LDA) to density-functional theory[10] with the Hedin-Lundqvist exchange-correlation potential is used. We have calculated the theoretical equilibrium volume Ω_0 of the *W* phase by total-energy minimization of the ideal structure, i.e., $c/a=(\frac{8}{3})^{1/2}$ and $u=\frac{3}{8}$: We obtain in this way $\Omega_0=181.28$ a.u. For the distorted wurtzite structure, an energy-minimization process over the three independent parameters *a*, *c*, and *u* is affected by computational noise, and does not give reliable results for all parameters; we have therefore assumed for the actual structure the experimental[8] values $c/a=1.623$ and $u=0.3785$, while keeping the volume Ω_0 of the ideal case. Such a hybrid choice is not new and gave satisfactory results in other works;[9,17] it corresponds to *a* and *c* values which are only 1% smaller than experimental ones.[8] Furthermore, recent work has pointed out the importance of using *theoretical* equilibrium volumes when dealing with macroscopic electrostatics.[5] For a given choice of the *W* parameters, there is a unique lattice-matching parameter for the cubic ZB phase.

Calculations have first been performed for a supercell where the *W* slab has the ideal geometry. We notice that the calculated density and potential are periodic in the planes perpendicular to the *c* axis, and the relevant information is contained in their planar averages $\bar{n}(z)$ and $\bar{V}(z)$. As a further tool to blow up quantities related to electrostatics, we use the concept of macroscopic average recently introduced by some of us in the context of heterojunctions.[14,15] The periodic part of the microscopic oscillations is filtered out by performing the convolution $\bar{\bar{n}}(z)=(1/l)\int_{z-l/2}^{z+l/2}dz'\bar{n}(z')$ [and analogously for $\bar{\bar{V}}(z)$], where $l=c/2$ is the period along *z* of the planar averaged functions. Since convolution commutes with the Poisson equation, the macroscopically averaged charge and potential coincide in the bulklike regions with the corresponding quantities of macroscopic electrostatics.

The lower panel of Fig. 1 displays the valence electron density and the corresponding potential energy. The interfaces occur where $\bar{\bar{n}}(z)$ significantly deviates from constancy, and they are well localized around the conventional positions defined above. In the central region of both slabs, $\bar{\bar{n}}(z)$ is constant, and $\bar{\bar{V}}(z)$ is linear. This confirms that our layer superstructure is thick enough for reproducing bulk *macroscopic* features. The narrow width of the interfaces is in agreement with the current findings for most semiconductor heterojunctions.[15] Basically, this owes to the fact that no dangling bonds are present, and that no interface states occur in the fundamental bulk gaps. Furthermore, it is known that the total electronic charge density recovers its bulklike value on a much shorter distance from the interface than the one-electron density of states.

The two interfaces have a nonvanishing surface charge. Since they are well separated, the macroscopically averaged surface charges will not be modified appreciably by increasing the supercell size. Incidentally, this problem has been faced earlier, with similar tools and results, for a different kind of charged interfaces.[18] The macroscopically averaged potential $\bar{\bar{V}}(z)$ increases linearly in the *W* region, and drops back to its initial value in the ZB region, in order to ensure the supercell periodicity. In fact, the potential $\bar{\bar{V}}(z)$ and the corresponding macroscopic electric field $E_3(z)$ depend on the local charge distribution *and* on the boundary conditions.[4] Here the average field over the whole supercell vanishes, but nonzero fields, of opposite sign, are present in the two slabs separately; the equations of macroscopic electrostatics imply that the *difference* between the macroscopic electric fields in the two regions, which is proportional to the *difference* between the corresponding macroscopic polarizations, does not depend on the imposed boundary conditions.

Since ZB has no intrinsic bulk polarization, the appearance of fields is the fingerprint of spontaneous polarization in the W region: Its numerical value is $P_3 = -5.25 \times 10^{-3}$ C/m^2. This confirms that BeO has a spontaneous polarization in the ideal W structure, as it may be expected from symmetry considerations. The modest value of P_3 can be understood by considering that the polarization vanishes by symmetry in the ZB case, and that it is necessary to go to third neighbors of a given atom in order to find significant differences between ZB and ideal W.

We have performed a further check of the spontaneous nature of P_3 and of its bulklike character. Under a change of either the supercell size or the boundary conditions, the superlattice undergoes different macroscopic fields, hence different local-field *microscopic* polarizations result; such variations, however, should have no effect on the *macroscopic* quantity P_3. To prove this, we have added an external dipole layer in the ZB region of the supercell, such as it cancels the field in the W region. The self-consistent results prove that the macroscopic polarization difference between the two phases remains unchanged.

The supercell calculations have been repeated, replacing the ideal W slab by the distorted one. In this case, the ZB and W slabs have different interlayer distances along the c axis: This requires us to deal with the *total* (i.e., electronic and nuclear) charge density of the supercell, and to use the generalized definition of macroscopic average.[15] Apart from these differences, the computations have been performed along the same lines as described before. The resulting polarization, $P_3 = -1.52 \times 10^{-2}$ C/m^2, is about 3 times larger than in the ideal case. This enhancement of P_3 derives from the partial ionic character of the BeO bonds. The structural distortion, in fact, corresponds to moving ionic charges, i.e., to the creation of dipoles.

The spontaneous polarization of BeO has never been measured. Experimental data exist only for its variation induced, e.g., by temperature changes,[16] by strain,[16,19] or by a zone-center optical phonon.[20] In order to verify our computational scheme against experiment, and to demonstrate that our results are sound, we calculated the polarization **P** for a few values of $(c/a,u)$ at constant volume Ω_0. The results are summarized in Table I, and indicate that in the investigated range, P_3 is approximately a linear function of c/a and u with $\partial P_3/\partial(c/a)|_u = -0.06$ C/m^2, and $\partial P_3/\partial u|_{c/a} = -3.0$ C/m^2. In Fig. 2, we display the resulting constant polarization lines. The dependence of P_3 on u is 50 times stronger than on c/a. The strong variation of P_3 with u at fixed c/a can be checked against the experimental values[20] of the Born effective charges $|Z^*| = 1.85$. Assuming positive sign on cation and using[20] $\epsilon_\infty = 2.99$, we obtain $\partial P_3/\partial u|_{c/a} = 2Z^* ec/\Omega_0 \epsilon_\infty = -3.2$ C/m^2, which compares well with the above calculated value.

TABLE I. Spontaneous polarization (P_3) and corresponding macroscopic field (E_3) calculated in W BeO for different geometries at constant volume $\Omega_0 = 181.28$ a.u.

a (a.u.)	c (a.u.)	c/a	u	$10^{-9}E_3$ (V/m)	$10^2 P_3$ (C/m^2)
5.042	8.234	1.633	0.3750	0.59	−0.53
5.042	8.234	1.633	0.3785	1.78	−1.58
5.052	8.200	1.623	0.3785	1.72	−1.52
5.052	8.200	1.623	0.3765	1.05	−0.93

Finally, we present a consistency check of our results based on the measured values[16,19] of the piezoelectric stress coefficients $e_{31} = -0.051$ C/m^2 and $e_{33} = 0.092$ C/m^2. We consider the stress which, at $\mathbf{E} = \mathbf{0}$ and constant volume, transforms the measured c/a ratio into its ideal value. Such a stress produces a variation of polarization

$$\Delta P_3 = e_{31}(S_1 + S_2) + e_{33} S_3 = 5.86 \times 10^{-4} \text{ C/m}^2,$$

given the strain $S_1 = S_2 = \Delta a/a = -2.05 \times 10^{-3}$ and $S_3 = \Delta c/c = 4.10 \times 10^{-3}$. Besides a variation of c/a, the stress produces also an internal strain Δu which is not known experimentally, since such a measurement is very delicate,[21] but which dominates ΔP_3. According to our theoretical results, the above value of ΔP_3 implies

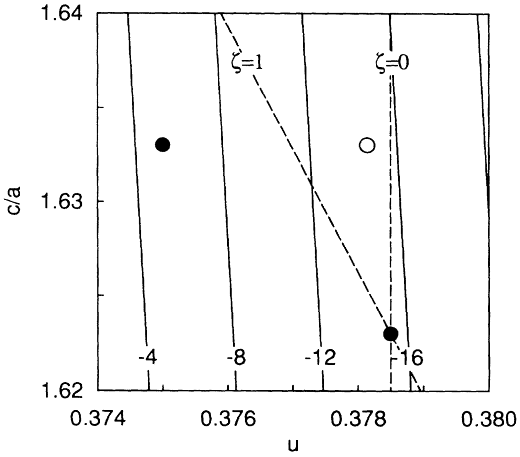

FIG. 2. Predicted equipolarization lines for W BeO in the $(c/a,u)$ plane at constant unit-cell volume Ω_0. Polarization is given in units of 10^{-3} C/m^2. Solid circles indicate ideal and distorted structures. The two broken lines correspond to strained experimental structures with complete bond bending ($\zeta = 1$) and without internal strain ($\zeta = 0$). The meaning of the open circle is explained in the text.

$\Delta u \simeq -3.6\times 10^{-4}$, corresponding to a *bond-bending* constant[22] $\zeta \simeq 0.2$ which is in the physically meaningful range $0 \leq \zeta \leq 1$. This is represented in Fig. 2, where the broken lines $\zeta = 0$ and $\zeta = 1$ delimit the physical range, and the open circle gives the predicted crystallographic parameters of BeO under the assumed stress.

In conclusion, our study of wurtzite BeO shows that the electronic term of the spontaneous macroscopic polarization of solids can be obtained with sufficient accuracy from state-of-the-art all-electron calculations. We hope that this will open the way to fully quantum-mechanical treatments of pyroelectricity and ferroelectricity.

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[1] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, London, 1960).

[2] R. Resta, in *Festköperprobleme,* edited by P. Grosse (Vieweg, Braunschweig, 1985), Vol. XXV, p. 183; S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).

[3] R. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B **1**, 910 (1970); S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[4] R. M. Martin, Phys. Rev. B **5**, 1607 (1972).

[5] S. de Gironcoli, S. Baroni, and R. Resta, Phys. Rev. Lett. **62**, 2853 (1989).

[6] A. Scharmann and G. Schmirler, Phys. Status Solidi (a) **97**, 265 (1986).

[7] J. L. Birman, Phys. Rev. **109**, 810 (1958).

[8] D. K. Smith, H. W. Newkirk, and J. S. Kahn, J. Electrochem. Soc. **111**, 78 (1964).

[9] K. J. Chang, S. Froyen, and M. L. Cohen, J. Phys. C **16**, 3475 (1983); K. J. Chang and M. L. Cohen, Solid State Commun. **50**, 487 (1984).

[10] *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[11] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984).

[12] R. M. Martin, Phys. Rev. B **9**, 1998 (1974).

[13] J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. B **22**, 2060 (1980); J. E. Northrup and M. L. Cohen, Phys. Rev. B **23**, 2563 (1981).

[14] A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).

[15] S. Baroni, R. Resta, A. Baldereschi, and M. Peressi, in *Spectroscopy of Semiconductor Microstructures,* edited by G. Fasol, A. Fasolino, and P. Lugli, NATO Advanced Study Institutes, Ser. B, Vol. 206 (Plenum, New York, 1990).

[16] S. B. Austerman, D. A. Berlincourt, and H. H. A. Krueger, J. Appl. Phys. **34**, 339 (1963).

[17] A. Qteish and R. Resta, Phys. Rev. B **37**, 1308 (1988).

[18] K. Kunc and R. Resta, Phys. Rev. Lett. **51**, 686 (1983); R. Resta and K. Kunc, Phys. Rev. B **34**, 7146 (1986).

[19] *Landolt-Börnstein: Elastic, Piezoelectric and Related Constants of Crystals,* edited by O. Madelung (Springer-Verlag, Berlin, 1979), Vol. III/11, p. 370.

[20] E. Loh, Phys. Rev. **166**, 673 (1968).

[21] C. S. G. Cousins, L. Gerward, J. S. Olsen, B. Selsmark, and B. J. Sheldon, J. Phys. C **20**, 29 (1987); Semicond. Sci. Technol. **4**, 333 (1989).

[22] L. Kleinman, Phys. Rev. **128**, 2614 (1962).