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Elastic constants, phase transition, and electronic structure of strontium oxide SrO: An *ab initio* Hartree-Fock study

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The static structural properties and $B1$-$B2$ phase transition of SrO were calculated at an *ab initio* level within the Hartree-Fock (HF) approximation using the effective core potential. The HF data were corrected *a posteriori* by integrating the HF charge density according to the correlation—only gradient-density-functional formulas proposed by Colle and Salvetti [Theor. Chim. Acta **37**, 329 (1975)] and by Perdew [J.P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992)]. The HF binding energy, structural parameters, lattice parameter, bulk modulus, and elastic constants are in reasonable agreement with experiment. The correlation correction brings the binding energy into better agreement with the experiment. The transition pressure between $B1$ and $B2$ phases is in good agreement with the experimental value at the HF level, whereas it is corrected poorly by the addition of an *a posteriori* correlation correction.

I. INTRODUCTION

The *ab initio* self-consistent-field Hartree-Fock linear-combination-of-atomic-orbitals (SCF-HF-LCAO) computational method may be used to solve one-particle electronic equations using periodic boundary conditions: The crystalline orbitals are expanded into a basis set of Gaussian-type functions (GTF's). The method is described in detail in Refs. 1–3, and is implemented in the program CRYSTAL,[4,5] which can treat periodic systems in one, two, and three dimensions. The inclusion of effective core potentials (ECP's) (Refs. 6–9) allows us to apply the method to compounds containing elements belonging to the periods from 4 to 6. The ECP-HF-LCAO method has been applied to a large set of semiconductors,[10] giving binding energies and geometries in good agreement with experiment.

The description of the electronic structure of crystals obtained by the one-electron Hartree-Fock Hamiltonian can be improved by including interparticle correlations. We calculate the correction to the energy by integrating the Hartree-Fock electronic density[11,12] according to the correlation gradient-density functional (DF) proposed by Colle and Salvetti[13] (CS) and Wang and Perdew (WP91):[14] This method has already been tested to improve the binding energies and the equilibrium lattice parameters of covalent systems[10] and of layered crystals such as $Mg(OH)_2$ (Ref. 15) and $MgCl_2$.[16]

Recent improvements in the accuracy of the CRYSTAL program allow us to study the structural features of ionic crystals, such as the lattice equilibrium parameter, the binding energy, the elastic constants,[17] and the transition between $B1$ (fcc) and $B2$ (bcc) phases.[18,19] In all the cases mentioned it may be observed that the equilibrium lattice parameters and the transition pressures of the ionic crystals are in good agreement with the experimental data.

The objective of the present work was to study the structural features of strontium oxide and the effect of the correlation correction: In this respect the pressure transition between $B1$ and $B2$ phases is a very good indicator of the accuracy of the calculation. At the same time we wanted to verify if the ECP approximation adds any additional error in the description of the electronic properties and if the use of the correlation correction of the energy by density functionals gives the right correction to the structural data.

SrO has been studied in many experimental and theoretical works. Sato and Jeanloz[20] measured the $B1$-$B2$ phase transition. Chang and Graham,[21] Son and Bartels,[22] and Michard and Zarembowitch[23] measured the elastic constants with ultrasonic techniques; Bartels and Vetter[24] measured the temperature dependence of the elastic constants, allowing extrapolation of the measured values to the athermal limit. Taurian, Springborg, and Christensen[25] studied the electronic structure of the $B1$ phase with the linearized-muffin-tin-orbital method, within the local-density approximation of von Barth and Hedin.[26] Pandey, Jaffe, and Kunz,[27] in a recent paper, calculated the electronic structure following the Adams-Gilbert-Kunz (AGK) localized-orbital-Hartree-Fock method. Zhang and Bukowinski[28] calculated the $B1$-$B2$ transition pressure using a modified-electron-gas model. The target of the present calculation was to investigate what level of accuracy can be

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reached by applying a fully periodic crystalline-orbital LCAO Hartree-Fock method to a heavy ionic crystal.

II. METHOD OF CALCULATION

The feasibility of the Hartree-Fock periodic calculation is intrinsically linked to the numerical approximations introduced in the treatment of the infinite series of Coulomb[29] and exchange[30] integrals, and in sampling and interpolating the quantities defined in the reciprocal space,[31] where the effective Hamiltonian matrices are diagonalized. According to the experience gained in the calculations performed on ionic crystals,[2,3,32,33] we are able to control the approximations in the present situation in such a way that the relative errors in the binding energy, the equilibrium lattice parameter, and elastic constants are below 0.3%, 0.1%, and 0.5%, respectively.

The basis set used in this calculation is reported in Table I. The use of the effective core potentials reduces the dimension of the basis set and avoids the difficulties in describing the core cusps of heavy atoms: Gaussian ECP's (Refs. 7 and 8) have been successfully applied to a large set of covalent[10] and ionic crystals.[34] The frozen core approximation gives poor results when applied to alkaline and alkaline-earth compounds;[35,7] this happens also in the case of compounds with Sr, which has the electronic configuration $[1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6] 5s^2$. To overcome this problem we applied the small-core approximation:[7] Instead of putting all the electrons belonging to the core (square brackets) into the ECP, we included explicitly in the calculation the electrons belonging to the Sr 4*sp* shell, the most external of the core. Therefore the ECP substitutes only the 1*s*, 2*sp*, and 3*spd* electrons of Sr, making the assumption that all the effects of core polarization will be confined in the 4*sp* shell. Small-core ECP's have been calculated by Hay and Wadt[7] for the elements belonging to groups IA to IB of the periodic table.

We used a double-ζ quality GTF basis set, which is reported in Table I. One set of *d* functions was added to the Sr centers to increase the ion flexibility. The exponents and coefficients of the oxygen basis set were fully optimized in the study of CaO;[19] the exponent of the most diffuse orbital was reoptimized in this study. The basis set for Sr is new and was fully optimized for use in bulk. The *d* polarization functions were taken from the CaO study and scaled by an optimized factor. The *d* orbitals play a critical role in the choice of the basis set. Although their population is small (0.085), their influence on binding energy, structural parameters, and elastic constants is far from negligible: The binding energy increases by 0.03 hartree, the equilibrium parameter contracts by 0.026 Å, whereas the bulk modulus increases by 5 GPa.

It is well known from molecular calculations that the HF method underestimates the binding energies by about 30%, whereas the bond lengths are overestimated by 0.5–1 % (Ref. 36) in covalent systems. Similar results were obtained in a systematic study of III-V semiconductors.[37,10] The situation is more complex in ionic crystals: The ions are stabilized by the lattice Coulomb forces, so that the local electronic structure is far from that of the isolated atoms and also slightly different from the isolated ions. The correlation errors on the structural parameters of ionic systems are not systematic, although they increase regularly with the dimensions of the anions.[34,32]

In this situation it is interesting to evaluate the effect of the correction of the energy-related quantities by integrating the correlation-only density functionals as a functional of the Hartree-Fock electronic density.[11] A numer-

TABLE I. Basis set as used in the present study. The Hay-Wadt small-core pseudopotential was used on strontium. The effect of 4*d* polarization functions on strontium was studied, as explained in the text.

	Strontium				Oxygen		
Shell	Exponents	Coefficients		Shell	Exponents	Coefficients	
type		*p* or *d*	Type		*s*	*p*	
4*sp*	3.244	2.32(-1)	-1.29(-1)	1*s*	4.000(+3)	1.44(-3)	
	2.403	-7.09(-1)	5.05(-2)		1.356(+3)	7.64(-3)	
	6.933(-1)	8.31(-1)	6.37(-1)		2.485(+2)	5.37(-2)	
					6.953(+1)	1.68(-1)	
					2.389(+1)	3.60(-1)	
					9.276	3.86(-1)	
					3.820	1.47(-1)	
					1.235	7.11(-2)	
5*sp*	2.577(-1)	1.000	1.00	2*sp*	5.219(+1)	-8.73(-3)	9.22(-3)
					1.033(+1)	-8.98(-2)	7.07(-2)
					3.210	-4.08(-2)	2.04(-1)
					1.235	3.77(-1)	3.49(-1)
					5.364(-1)	4.22(-1)	2.78(-1)
4*d*	3.191		1.60(-1)	3*sp*	1.814(-1)	1.00	1.00
	8.683(-1)		3.13(-1)				
	3.191(-1)		4.06(-1)				

ical integration scheme was adopted, based on a generalization to periodic systems of the atomic centred methods proposed by Becke[38] and Savin[39] for molecules. This method can confine the relative error in the integrated charge to within 0.01%, corresponding to a maximum error of 0.0005 hartree per unit cell in the correlation energy.

For the uncompressed crystal the calculation of the total energy and the wave function took 125, 2, and 16 s of Cray YMP 116 CPU time for the evaluation of the integrals over GTF functions, the self-consistent-field process, and the density-functional energy correction, respectively.

III. *B*1 PHASE: STRUCTURE AND ELECTRONIC PROPERTIES

The total and projected densities of the states are shown in Fig. 1. As expected for ionic oxides, the gaps are large and the contribution to the valence band is mainly due to the *p* bands of oxygen. The valence-band width is 2.38 eV, which is almost the same value as 2.39 eV obtained by the LDA-LMTO method[25] and half the value of 4.35 eV obtained by the Adams-Gilbert-Kunz (AGK) HF method:[27] This result is coherent with that obtained for LiH by Asthalter *et al.*,[40] where crystalline-orbital LCAO and AGK methods were compared. We expect that our value of the bandwidth is not more than 10% larger than the experimental one, as may be inferred from Ref. 33. In our case the 4*p* states of strontium and 2*s* of oxygen overlap, whereas in Ref. 27 they are separated. We believe this is the effect of correlation. The topology of the band structure confirms the ionic picture of the crystal with flat bands and large gaps. The gap between the valence and conduction bands is overestimated in the Hartree-Fock model, as discussed by Pandey, Jaffe, and Kunz[27] for the alkaline-earth oxides: Work is in progress to correct not only the total energy, but also the wave function, taking into account the correlation effects.

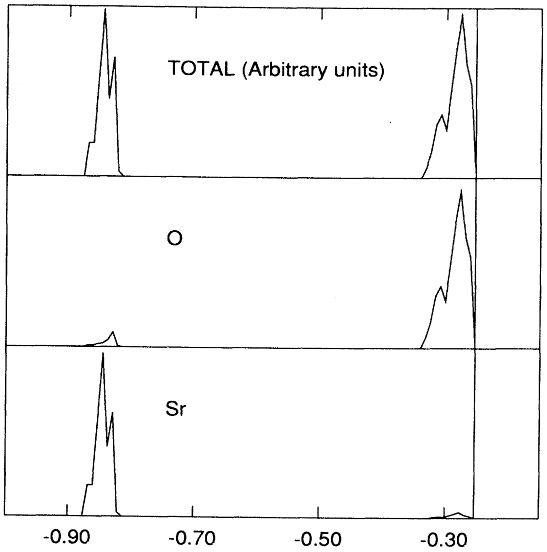

FIG. 1. Density of states. Total density and projected densities to single atoms are plotted in arbitrary units. E_f denotes the Fermi energy.

A Mulliken electron-population analysis was performed for the equilibrium lattice parameter (Table II). Although arbitrary, it often gives reliable information about the relative ionicity of similar compounds if calculated with very similar basis sets: The net charge of O is 1.95, 1.83, and 1.94 for MgO,[33] CaO,[32,19] and SrO, respectively, indicating that Mg and Sr oxides are nearly totally ionic and slightly more ionic than CaO. As expected for ionic compounds there is a very small antibonding population ($-0.051|e|$) between cation and anion. In this respect it is interesting to consider the effect of isotropic compression on the detailed ion-charge distribution (Table II). For a decrease of the cell edge from 5.23 to 4.92 Å, the total electron charges hardly change, indicating ionic bonding even in a compressed situation. A transfer of charge is observed from Sr 5*sp* to 4*d* orbitals, showing the importance of *d* functions in the calculation of elastic properties. The electronic rearrangement due to compression causes a transfer of charge from the 2*sp* to 3*sp* orbitals of oxygen.

Figure 2 presents the difference electronic density plot: The electronic density of isolated atoms was subtracted from the crystal density. The electronic distribution around the ions clearly departs from spherical symmetry, underlining the importance of ionic polarization. Electronic charge accumulates in the valence region of oxygen, the core region being practically unchanged. The corresponding lack of charge in the valence region of Sr cannot be observed, because the valence region of the isolated Sr atom is far too expanded and overlaps with the anion positions.

Two different reactions were considered to calculate the binding energy:

TABLE II. Effects of isotropic compression of the cell edge *a* on the shell charges ($|e|$) of Sr and O, which are evaluated according to the Mulliken partitioning scheme. Shell symbols refer to Table I.

	a (Å)	5.23	5.07	4.92
Sr	4*sp*	4.606	4.603	4.600
	5*sp*	3.371	3.360	3.348
	4*d*	0.085	0.098	0.112
	Total	8.062	8.061	8.060
O	1*s*	2.007	2.007	2.007
	2*sp*	4.644	4.664	4.685
	3*sp*	3.287	3.269	3.249
	Total	9.938	9.929	9.940

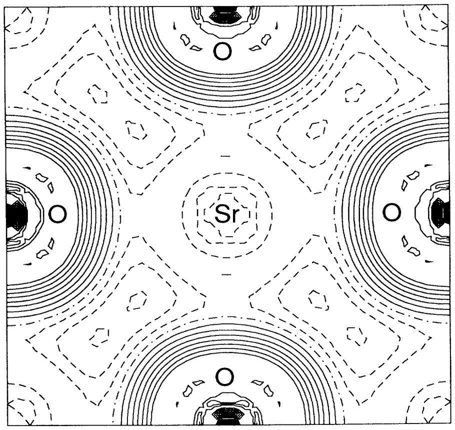

FIG. 2. Differential electron-density map. The difference between two isolines is 0.002 a.u. in the range from −0.006 to 0.026 a.u. Dashed lines represent negative values and the dot-dashed line represents the zero line.

$$Sr_g + O_g \longrightarrow SrO_c, \tag{1}$$

$$Sr_g + O_g \longrightarrow Sr_g^{2+} + O_g^- + e^-, \tag{2a}$$

$$Sr_g^{2+} + O_g^- + e^- \longrightarrow SrO_c. \tag{2b}$$

For reaction (1) the energies of the free atoms were calculated by modifying the ionic basis set used for the crystal: For oxygen the $3sp$ shell (Table I) was substituted by three separate sp shells with the exponents 0.45, 0.285, and 0.115 bohr^{-2}; for strontium the $5sp$ shell was in the same way substituted by three separate sp shells with exponents 0.27, 0.18, and 0.035 bohr^{-2}. To evaluate the energy corresponding to reaction (2a), we used the experimental ionization potentials of Sr and the electronic affinity of O.[41] The advantage of reaction (2a) with respect to (1) lies in a greater homogeneity between the optimal basis sets for reactants and products, which are both in the ionic state: The free O^- ion was obtained by optimizing the external $3sp$ shell of the basis set from Table I, giving $\alpha = 0.1905$ bohr^{-2}. O^- was used instead of O^{2-}, because no stable Hartree-Fock wave function for O^{2-} exists. The data used in evaluating the binding energy are reported in Table III. The total energy of the crystal refers to the equilibrium lattice parameter (Table V). The experimental binding energy was evaluated by following the Born-Haber thermochemical cycle, using the data reported in Refs. 41–43. The zero-point vibration energy data was added. Table IV reports the results for reactions (1) and (2a): In any of the cases reported in Tables III and IV the difference between the data calculated by the two gradient-corrected functionals is significant. As expected, the Hartree-Fock method underestimates the binding energies by 40%. Including the correlation density-functional *a posteriori* correction, the energies are underestimated by 20% using atomic references [reaction (1)] and by 10% using ionic references [reaction (2b)]. This error is in line with other results on ionic crystals[32] and is larger than the error of the calculated binding energy of covalent systems (3% on the average[10]). The comparison of data in Tables III and IV suggests the hypothesis that the dominant error is the inadequacy of the model in the description of the correlation in the ions: In reaction (2b) error is introduced both in the reactants (O^- ion) and in the product (O^{2-} in SrO crystal), and so it is partially canceled. On the other hand, in reaction (1) the error is introduced only in the product, and so the binding energy is more underestimated. The calculated ionization energies reported in Table III support this hypothesis: The ionization potential of strontium is underestimated by about 0.5 eV, while the electronic affinity of oxygen is underestimated by 1 eV. The correlation correction of electron affinity operated by the present model is negative: The absolute value of the DF correlation energy calculated for the O^- ion is less than that energy calculated for O the atom.

We believe there are two reasons for this error. First, the two functionals are themselves only an approximation to the real correlation energy; and second, we made a certain approximation by taking the HF density as the starting point for the correlation correction. Namely, WP91 is a functional of the Kohn-Sham electronic density and its gradient. The use of the HF density certainly introduces a large error for anions where the HF density is sensitively different from the correlated one. On the other hand, the CS functional is a functional of a HF density. But the basic hypothesis of this functional, especially the width of the Wigner hole, is less valid when the ground state cannot be well represented by a single determinant: For such

TABLE III. Detailed results of energies, used in reactions (1) and (2) to obtain the binding energy. *A posteriori* correlation corrections were made to the energy using Colle-Salvetti (HF+CS) (Ref. 13) and Wang and Perdew 91 (HF+WP91) (Ref. 14) correlation functionals. The values are in hartrees, if not otherwise indicated.

	Expt.[a]	HF	HF+CS	HF+WP91
SrO		-105.137514	-105.876950	-105.946174
Sr		-30.101033	-30.367513	-30.427783
O		-74.794087	-75.065037	-75.061787
Sr^{2+}		-29.544680	-29.769330	-29.838050
O^-		-74.751422	-75.055080	-75.053450
IP_1+IP_2 (eV)	16.725	15.138	16.276	16.047
EA (eV)	1.461	1.161	0.271	0.2268

[a] Reference 41.

TABLE IV. Binding energy of SrO evaluated according to reactions (1) and (2). The values are in kcal/mol. The experimental value of 240.8 kcal/mol was obtained by following the Born-Haber thermochemical cycle, as described in the text.

	HF	HF+CS	HF+WP91
Reaction (1)	152.1	192.6	200.7
Reaction (2)	176.0	222.2	224.0

applications the authors recommend applying a modified functional to a multiconfigurational wave function.[13] Unfortunately, this is at the moment out of the scope of our method.

At present we are modifying the program to include the DF correlation corrections self-consistently, which would produce a correlated density and would also enable us to study the effect of full nonlocal exchange-correlation potentials.

Calculation of the elastic constants is a very efficient test of the quality of the calculated wave function. Two sets of experimental data for C_{11}, C_{12}, and C_{44} adiabatic constants of SrO were considered. The first set[22] was obtained using the ultrasonic pulse-echo technique at room temperature, and the second by the ultrasonic standing-wave technique.[23] The two sets of adiabatic constants are relatively similar.

To compare these data to the present theoretical result, the experimental elastic constants at the athermal limit were found by extrapolating back to 0 K using the temperature derivatives of the elastic constants given in Ref. 24.

Using the atomic basis set in Table I, the total energy of SrO was calculated for a number of different deformations of the unit cell. The variation of energy values versus strain components η_i were fitted to a polynomial function up to the sixth order. Thus the second derivatives of energy at the equilibrium lattice parameter could be calculated and the elastic constants are given by the relation (valid at 0 K)

$$C_{ij} = \frac{1}{V}\left[\frac{\partial^2 E}{\partial\eta_i \partial\eta_j}\right], \tag{3}$$

where V is the volume of the crystallographic unit cell. The Voigt convention for the stress components was adopted.

By simply changing the edge a of the unit cell, isotropic deformation of the crystal structure was attained, which gave the equilibrium value of a at zero stress (minimum point of energy) and the bulk elastic modulus B (second derivative of the energy at the minimum point). The energy was computed for 12 values of the lattice parameter in the range from 5.00 to 5.40 Å. Least-square fits were performed on polynomials for the function $E(a)$. The equilibrium value is practically independent of the order of the polynomial and also B shows a good stability to variation in the fitting function.

The calculated equilibrium lattice parameter a_0 is 5.23 Å, which is to be compared with experimental value of 5.16 Å.[44] As expected, the correlation correction contracts the values of the lattice parameter to 5.10 and 5.06 Å for the CS and WP91 correlation corrections, respectively.

Values of the elastic constants C_{11} and $C_{11} - C_{12}$ were calculated by applying the deformations $[\eta, 0, 0, 0, 0, 0]$ and $[\eta, \eta, -2\eta, 0, 0, 0]$, respectively. The first deformation corresponds to contracting one edge of the cubic cell, while the second to contracting two and stretching one edge by a double amount. For each of these deformations, the second derivative of energy with respect to the single parameter η needs to be calculated, as it comes from the second-order expansion of the elastic energy:

$$E = \frac{1}{2}\sum_{1}^{6} C_{ij}\eta_i\eta_j. \tag{4}$$

This reduces the number of CRYSTAL runs when compared to the straightforward formula (3), which involves the computation of mixed derivatives. Fourteen values of η were used, corresponding to changes of cell edges in the range ±0.16 Å around the equilibrium lattice parameter.

The corresponding value of the bulk modulus $B = (C_{11} + 2C_{12})/3$ is 108 GPa and is the same as the value derived independently by the least-squares fit of $E(a)$ to the $[\eta, \eta, \eta, 0, 0, 0]$ deformation.

In order to calculate the shear elastic constant C_{44}, the $[0, 0, 0, \eta, \eta, \eta]$ lattice strain was considered, corresponding to rhombohedral deformation of the cubic unit cell. The α, β, and γ angles increase ($\eta < 0$) or decrease ($\eta > 0$) by the same quantity, according to compression or stretching along the $[1, 1, 1]$ diagonal. Fourteen η values, ranging between -0.15 and 0.15 were considered.

The values are reported in Table V. The value of lattice parameter is 1.7% higher than the experimental one, but is in the range of expected error for a HF calculation. The presence of d polarization functions contracts the value of the lattice parameter by 0.3%. More important is the presence of d functions in the calculation of elastic constants. We explain this by considering that electrons are much more polarized when anisotropic deformation is applied to the crystal cell than in the case of isotropic deformation (calculation of the lattice parameter). All the values for elastic constants calculated with d functions have the errors in the same range and of the same

TABLE V. Table of lattice and elastic constants. The value for the lattice parameter a_0 is in Å, whereas the values for elastic constants C_{11}, C_{12}, C_{44}, and B are in GPa. The errors are calculated with respect to the first set of experimental data. BS and BS+d denote the basis set from Fig. 1 without and with d polarization functions, respectively. The experimental lattice parameter a_0 is from (Ref. 44) at 298 K.

	Experimental		BS	BS+d	Δ % BS	Δ % BS+d
	Ref. 22	Ref. 23				
a_0	5.16		5.25	5.23	+1.7	+1.4
C_{11}	183.2	175.4	228	219	+25	+20
C_{12}	47.1	44.4	45	52	-5	+10
C_{44}	57.7	54.3	75	72	+30	+25
B	90.6		106	108	+17	+19

sign. We justify these errors, averaging 20%, from experience with molecular calculations. The corresponding quantities in molecules are the IR vibrational frequencies. Values for these frequencies that are in good agreement with experimental ones are obtained only in cases when a triple-ζ basis set is used on the atoms and the dynamical correlation is included. In the case of a double-ζ basis set and without the correlation estimations, the errors are around 20% (Ref. 36, Chap. 6.3, p. 226). This is also the case in our study, where only a double-ζ basis set was used on oxygen and polarization functions only on strontium. The introduction of a triple-ζ basis set would enormously increase the computational effort, introduce the problems of linear dependence of atomic orbitals, and cause a catastrophic behavior of the program.[1] Also we have no means to estimate the contribution of the dynamic correlation.

IV. $B1$-$B2$ PHASE TRANSITION

A phase transition of the first order in SrO from the $B1$ (fcc) to $B2$ (bcc) phase was reported in Ref. 20 at the pressure of 36 ± 4 GPa. The decrease of the volume of the crystalline unit cell at the transition was 13%.

In the theoretical study the behavior of the free energies of both phases was considered. Free energy in our case is a function of lattice parameter:

$$G(a) = E(a) + p(a)V(a) = E(a) - \frac{\partial E(a)}{\partial V(a)}V(a). \quad (5)$$

In order to obtain an analytical expression for $G(a)$, least-squares fits were performed to polynomials up to the seventh order for the function $E(a)$. The energy was calculated at 40 points with different lattice parameters for both phases in the range from 4 to 6 and 2.5 to 5 Å for the $B1$ and $B2$ phases, respectively. For the first time in the study of phase transitions, the basis set in Table I without the d functions was optimized at each point (the exponents of the most diffuse Gaussians were allowed to relax). The difference between the fixed and point-optimized basis set is small (see Table VI) and does not justify the computational effort. The phase transition was also calculated with the complete basis set from Table I, but no optimization was performed at each point, following the experience gained from the previous case.

From the analytical expression for the energy $E(a)$, free energies were computed for both phases and plotted against pressure (Fig. 3). The intersection of the curves gives the transition pressure, as reported in Table VI.

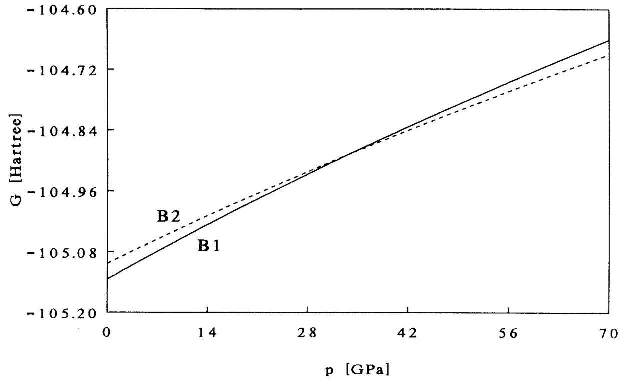

FIG. 3. Plot of free energy vs pressure for $B1$ (solid line) and $B2$ (dashed line) phases. The $B1$ phase is stable from zero pressure up to the transition point and the $B2$ phase is stable at higher pressures.

TABLE VI. Table of phase transition data. In the first row the transition pressure is given, in the second the change of volume of the unit cell at the transition. The data in different columns were obtained with different basis sets, as discussed in the text.

	Expt.[a]	Fix. BS	Opt. BS	Fix. BS+d	Calc.[b]
p (GPa)	36±4	39.4	41.5	33.5	35
ΔV (%)	-13	-12.3	-11.5	-12.8	-10

[a] Reference 20.
[b] Reference 28.

The stability of the transition pressure and decrease of volume were tested against the order of the fitting polynomial and the number of points. Good stability was obtained, with an estimation of the error to 0.5 GPa and 0.5% in the transition pressure and decrease of volume, respectively.

In Fig. 4 the calculated adiabates compared to the experimental values[20] are presented. The calculated curves overestimate the volume at a given pressure by an average of 12%. This is a consequence of the well-known inconsistencies of the HF method in the volume of the unit cell and the pressure $[-\partial E(a)/\partial a]$, which are overestimated by 5% and 7%, respectively, as seen in the study of the elastic constants. This error does not come up in the calculation of the transition pressure, since it is present in both phases equally and cancels out when the intersection of free energies for both phases is sought in the V versus p diagram.

The calculated values for the transition pressure both

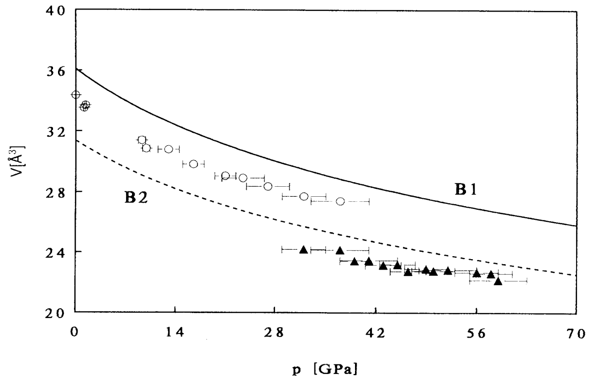

FIG. 4. Plot of adiabates for $B1$ (solid line) and $B2$ (dashed line) phases. The experimental points (Ref. 20) are added with their experimental errors. The error in the experimental cell volume (y axis) is too small to be depicted.

TABLE VII. Effect of the correlation on the transition pressure. In the first two columns experimental and calculated transition pressure are given; in the third and fourth columns the experimental and calculated transition differences of energy, ΔE, are reported: The experimental value was calculated as $-p\Delta V$; in the fifth and sixth columns experimental and calculated transition differences of volume are given. Energies and volumes refer to a primitive unit cell.

	p (GPa)	ΔE (10^{-20} J)	ΔV (10^{-30} m^3)
Expt.[a]	36±4	12.9	-3.58
HF	33.5	12.6	-3.77
HF+CS	26.8	10.9	-4.07
HF+P91	20.5	10.0	-4.89

[a] Reference 20.

with and without polarization functions are within the experimental error, the former being in better agreement with experimental data both in the transition pressure and the change of volume.

The effects of the application of the *a posteriori* density-functional correction on the transition pressure are reported in Table VII: The correlation stabilizes the more compact $B2$ phase, shifting the transition pressure below the lower limit of the experimental uncertainty interval: The correlation introduces errors both in the transition difference of energy (about −20%) and in the transition difference of volume (+20%), as shown in the table. The dynamic correlation would introduce further relaxations of the electronic structure that are not taken into account within the present model.

V. CONCLUSIONS

In the present work the complete elastic tensor of an ionic crystal and a phase transition was computed by means of the *ab initio* LCAO-HF method, using effective core potentials: No extra errors were introduced by the ECP approximation with respect to other crystals studied by the all-electron HF method.

The application of an *a posteriori* correlation-only gradient-density functional gives reasonable correction to the binding energy; the absolute value of the error in the equilibrium lattice parameter is unchanged; the $B1$-$B2$ transition pressure is corrected poorly due to the inadequate description of the correlation in the anions. Work is in progress to introduce a correlation correction of the crystalline Hartree-Fock density matrix.

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