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Ab Initio Studies of Electronic Structure, Phonon Modes, and Elastic Properties of Mg₂Si

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The electronic structure, lattice parameters, phonon frequencies at the Brillouin zone center, and first-order elastic constants (C_{ij}) have been calculated at the ab initio Hartree–Fock level using either all-atomic-electron basis sets or basis sets associated with core pseudopotentials. Band structure, electronic density maps, and density of states have been plotted. The all-electron calculations point out a mixed covalent–ionic nature for the Mg–Si bonding. The need for flexibility and optimization of the atomic basis set is quantitatively assessed from a careful comparison of the results obtained using several different bases. This is necessary to describe correctly the variation of the potential energy surface of the crystal associated with atomic displacements due to lattice deformations. In the present calculations, the pseudopotential approximation is found to provide parameter values of practically similar quality as those of all-electron computations. The polarization orbitals are shown to have a fairly selective role for the calculation of the elastic constants, depending on the kind of strains involved (for instance, polarization on Si for C_{44} , polarization on Mg for the bulk modulus and C_{11}).

1. Introduction

Magnesium silicide Mg₂Si (Figure 1) is a cubic semiconductor that crystallizes in the antifluorite structure with one molecular unit per primitive cell and four formulas per fcc conventional cell (space group $Fm\bar{3}m$).¹ With its eight valence electrons per cell, it resembles much the more familiar group IV diamond and the III–V and II–VI zinc blende semiconductors. All of them display similar electronic structures, since the symmetries of their Bravais lattices and hence Brillouin zones are identical.

The properties of Mg₂Si have been extensively studied from the experimental point of view via X-ray diffraction,² photoemission spectroscopy,³ reflectivity,⁴ electrorefractivity,⁵ Raman scattering,⁶ IR absorption,⁷ and sound velocity.¹

Theoretical studies on the compound are scarcer. Up to now, only two sources can be found in the literature. The first one⁸ is a semiempirical pseudopotential determination of the electronic band structure. The second one⁹ is based on density functional techniques. It reports first-principles calculations of the cell parameter (a) and bulk modulus (B) that are found to be in moderate agreement with experimental results ($a = 6.16$ Å compared with the experimental value of 6.351 Å at 300 K; $B = 68$ GPa instead of the experimental value of 55 GPa).

The present paper intends to fill the demand for further theoretical data on Mg₂Si. It reports the results of calculations using the *ab initio self-consistent field Hartree–Fock linear combination of atomic orbitals* (SCF-HF-LCAO) computational method to determine the electronic structure, phonon modes, and elastic constants of magnesium silicide.

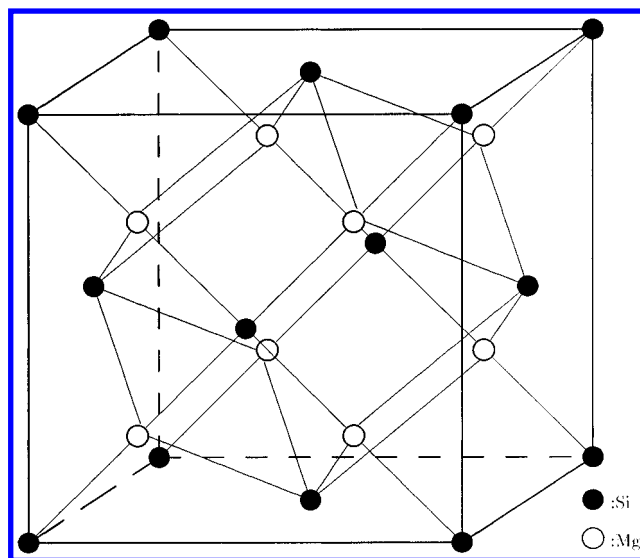


Figure 1. Antifluorite structure of the Mg₂Si semiconductor. Experimental lattice constant is $a = 6.351$ Å (300K). Space group is $Fm\bar{3}m$.

Besides the primary aim of providing ab initio data on Mg₂Si, special emphasis is put here on a study of basis set effects regarding various properties directly related to the electronic potential energy surface of the crystal. This methodological aspect of the paper will point out the possibility of using core pseudopotentials in the quantitative description of such properties through ab initio methods, though valence electronic charge densities seem to be significantly different in all-electron and pseudopotential calculations. It will also provide interesting information about the selective role of polarization functions.

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© Abstract published in *Advance ACS Abstracts*, October 1, 1997.

2. Methodology

The calculations were performed using the CRYSTAL-92 program that provides self-consistent field solutions (SCF) to the Hartree–Fock–Roothaan (HF) equations subject to periodic boundary conditions. Details of the mathematical formulation of this method can be found elsewhere.¹⁰ In this approach, the accuracy that can be achieved on the electronic energy depends on three types of approximations that propagate their effect to the calculated properties, lattice parameters, elastic constants, and phonon mode frequencies, through the numerical evaluation of the first and second energy derivatives.

The first of these approximations is inherent in the one-electron model that underlies the Hartree–Fock method; the electron correlation is ignored. However, this restriction is certainly much less severe for the properties calculated here than for others such as binding energies that are well-known to be very sensitive to differential correlation effects.

The second kind of approximation is related to numerical simplifications introduced in the implementation of the HF method in periodic solids. Thus, the infinite Coulomb and exchange series that contribute to the Fock matrix must necessarily be truncated (here, computational parameters controlling the truncation of both series have been chosen to obtain the standard “good” level of accuracy defined by Pisani, Dovesi, and Roetti¹¹). Moreover, the reciprocal space required for the SCF procedure must be discretized (a $8 \times 8 \times 8$ set of sampling k points in the irreducible Brillouin zone was used).

The third type of approximation is the unavoidable basis set incompleteness and the possible use of pseudopotentials. The basis sets used in CRYSTAL-92 calculations are composed of atomic orbitals (AO) that the crystalline orbitals are expanded into in the form of Bloch functions. Each AO is a linear combination of n Gaussian type functions (GTF's) that are products of a Gaussian $\exp(-\alpha r^2)$ and a real solid harmonic X_l^m . Indeed, the choice of the size and composition of the basis set is a crucial aspect of HF calculations. Previous studies using this methodology have shown that standard basis sets for molecular calculations must be modified to be suitable for calculations on periodic systems.¹¹

A number of basis sets were built for the present Mg_2Si calculations. The exponents were optimized through energy minimization of the crystal energy. Some of the bases tested in this work were all-electron basis sets, but most used Durand's and Barthelat's core pseudopotentials,^{12–15} and in this case the basis functions served to describe the valence orbitals only. In all cases, favoring the flexibility of the Si atomic basis proved to be efficient, since this center can be expected to bear practically all of the valence charge on the ground of elementary electronegativity considerations. From this point of view, calculations using all-electron basis sets should be considered as more reliable than calculations with pseudopotentials. For the sake of clarity and as a preparation for later discussions, we present the detailed results of the calculations for only three of the numerous basis sets tested. These three basis sets have been selected because the data they provide are representative of the principal trends found in this work. One of them is an all electron basis set (AE*) and the two others are basis sets associated with Durand–Barthelat pseudopotentials (PP* and PP) that just differ by the presence of Mg(p) and Si(d) polarization orbitals in the * basis (an asterisk conventionally means “with polarization orbitals” i.e., AO's of higher l values to allow for further deformation of the electronic cloud). These basis sets are given in Table 1. The exponents were determined through energy minimization except for the d orbital exponent that was fixed at 0.2 bohr^{-2} , since for a further decrease in α

of 0.1 bohr^{-2} the lowering in energy was less than 1 mhartree (≈ 0.4 mhartree). It will be shown below that this minor restriction does not alter significantly the values of the calculated parameters.

3. Results and Discussion

The values of lattice parameters, elastic constants, and phonon mode frequencies calculated with the three selected basis sets are given in Table 2. The Mulliken population analyses are reported in Table 3. These data are discussed in the rest of this section.

A. Crystal Structure. As noticed in the Introduction, Mg_2Si is known to have a cubic structure so that a single lattice constant “ a ” has to be optimized through the minimization of the crystal energy.

It is noted that the optimized value of the lattice parameter depends weakly on the basis set types and sizes. For all three selected basis sets, the bond length is slightly overestimated ($\approx 1\text{--}2\%$). This can be assigned partly to the fact that the HF approach disregards correlation effects and partly, when effective core pseudopotentials are used, to the neglect of the core polarizability. With basis sets not presented here, it was found that the presence of an AO of d symmetry on Si allowing for valence polarization results in a small decrease of the lattice parameter. Conversely, the presence of a p AO on Mg leads to an increase of this parameter.

B. Elastic Constants. The C_{ij} elastic constants and bulk modulus B have been calculated from the response of the electronic energy to suitable deformations, using the conventional method^{17,18} that was previously applied, among others, to the cubic fluorite CaF_2 ¹⁹ and antiferroite Li_2O ²⁰ or the tetragonal rutile-type MgF_2 .²¹ The energies calculated for a number of strains $[\eta_i, i = 1, 6]$ corresponding to appropriate deformations of the unit cell were fitted to polynomial functions up to fourth order. The elastic constants C_{ij} are given by

$$C_{ij} = \frac{1}{V_0} \left[\frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \right]_0$$

where V_0 is the volume of the primitive cell and the derivatives are evaluated at zero strain. Thus, the second derivatives of the energy at the energy minimum yield the elastic constants in the harmonic approximation.

$[\eta, \eta, \eta, 0, 0, 0]$ deformations have been employed for determining the bulk modulus B , $[\eta, 0, 0, 0, 0, 0]$ for C_{11} , $[\eta, \eta, 0, 0, 0, 0]$ for $C_{11} + C_{12}$, and $[0, 0, 0, \eta, \eta, \eta]$ for C_{44} . All these deformations correspond to external strains that lower the symmetry and may induce internal strains within the cell. These internal strains produce a relaxation of those atoms that acquire a structural degree of freedom in the external deformation. This is the case for the Mg atoms in the deformations used to calculate C_{44} ; they are relaxed out of the special $1/4$ position along the 3-fold axis. For example, with the PP* basis set, although the internal relaxation is small (0.00625 \AA for an external deformation of -2%), it is enough for decreasing the C_{44} value by as much as 10%.

Whereas the lattice constant is always fairly good, the tests show that a good flexibility in the basis set is absolutely required to calculate satisfactory values of the elastic constants of Mg_2Si . It was even found that the sp basis sets (i.e., time-earning bases in which s and p orbitals have the same exponents) that we tested for Mg_2Si were not appropriate for obtaining reliable results unless their sizes were extensively increased; thus, we reoptimized the outer exponents of the sp basis sets used by D'Arco et al.,²² but the elastic constants obtained with these

TABLE 1: Exponents (in bohr⁻²) and Contraction Coefficients of the Gaussian Functions Used for the Calculation of Various Properties of Antifluorite Mg₂Si as Described in the Text^e

atom		Gaussian basis sets				
		PP* ^c (PP) ^d		AE*		
		α^a	C^b	α	C_s	C_p
Mg, [Ne]3s ²	s			68371.9	2.600×10^{-4}	
				9699.34	1.8982×10^{-3}	
				2041.18	1.1045×10^{-2}	
				529.863	5.0663×10^{-2}	
				159.186	1.6912×10^{-1}	
				54.6848	3.6703×10^{-1}	
				21.2357	4.0041×10^{-1}	
				8.74604	1.4987×10^{-1}	
	sp			156.795	-6.2400×10^{-3}	7.7200×10^{-3}
				31.0339	-7.8820×10^{-2}	6.4270×10^{-2}
				9.64530	-7.9920×10^{-2}	2.1040×10^{-1}
				3.71090	2.9063×10^{-1}	3.4314×10^{-1}
				1.61164	5.7164×10^{-1}	3.7350×10^{-1}
				0.68	3.0664×10^{-1}	2.3286×10^{-1}
	s	4.342235	-1.3469×10^{-2}	2.882813	-1.3469×10^{-2}	
		0.176995	-1.34665×10^{-1}	0.356945	-1.34665×10^{-1}	
0.105560		1.	0.14	1.		
Si, [Ne]3s ² 3p ²	p	0.187298	1.	0.15	1.	
	s			16120.0	1.95900×10^{-3}	
				2426.00	1.49300×10^{-2}	
				553.900	7.285×10^{-2}	
				156.300	2.46100×10^{-1}	
				50.0700	4.85900×10^{-1}	
				17.0200	3.25000×10^{-1}	
				1.87905	2.02103×10^{-1}	
				1.53045	-4.29090×10^{-1}	
	sp			292.718	-2.78094×10^{-3}	4.4383×10^{-3}
				69.8731	-3.5715×10^{-2}	3.2667×10^{-1}
				22.3363	-1.1498×10^{-1}	1.3472×10^{-1}
				8.15039	9.3563×10^{-2}	3.2868×10^{-1}
				3.13458	6.0302×10^{-1}	4.4964×10^{-1}
				5.215953		1.
	s			1.18000		1.
2.649877		2.02103×10^{-1}				
1.637220		-4.29090×10^{-1}				
0.259431		1.	0.24	1.		
0.102906		1.	0.09	1.		
p	1.630182	1.				
	0.326227	1.	0.55		1.	
	0.092023	1.	0.14		1.	
	d	0.20	1.	0.20	1.	
total electronic energy in au						
PP*		-5.401265		valence electrons		
PP		-5.385369		valence electrons		
AE*		-685.772818		all-electrons		

^a α : exponent (in bohr⁻²). ^b C : contraction coefficient. ^c With polarization. ^d The PP basis set is the same as the PP* basis set minus the Mg(p) and Si(d) polarization orbitals. ^e The contraction coefficients multiply normalized individual Gaussians. The PP* and PP basis sets were used with Durand–Barthelat core pseudopotentials.^{12–15} Total electronic energies (in au) per cell are reported for each of the three selected basis sets.

bases were in deceptively poor agreement with experiment (for instance, B is 40% too large and things get even worse for the other constants). Basis sets with independent s and p exponents gave the best results. The three selected basis sets PP*, PP,

and AE* belong to this category. The results corresponding to these bases are reported in Table 2. They show that, whatever the basis set, C_{12} remains the less accurately calculated constant. This can be easily understood because it is calculated via a small

TABLE 2: Structural Properties and Elastic Constants and Raman and Infrared Frequencies Calculated with Selected Basis Sets (Labels Explained in Section 2)^a

	expt	PP*	PP	AE*
lattice constant (\AA)	6.338 ^{b,c}	6.506 $\Delta = +2.6\%$	6.427 $\Delta = +1.4\%$	6.430 $\Delta = +1.4\%$
bulk modulus B (GPa)	59 ^{b,c}	58 $\Delta = -1.6\%$	67 $\Delta = +14\%$	60 $\Delta = +1.6\%$
elastic constant C_{11} (GPa)	126 ^{b,c}	147 $\Delta = +17\%$	182 $\Delta = +44\%$	150 $\Delta = +19\%$
elastic constant C_{12} (GPa)	26 ^{b,c}	15.12 $\Delta = -41\%$	11.7 $\Delta = -55\%$	20 $\Delta = -23\%$
elastic constant C_{44} (GPa)	48.5 ^{b,c}	45.4 $\Delta = -6\%$	57.9 $\Delta = +19\%$	58.2 $\Delta = +20\%$
Raman frequency ν_R (cm^{-1})	258.5 ^{b,c}	280 $\Delta = +8\%$	335 $\Delta = +30\%$	284 $\Delta = +10\%$
infrared frequency ν_{IR} (cm^{-1})	267 ^{b,c}	251 $\Delta = -6\%$	312 $\Delta = +17\%$	272 $\Delta = +2\%$

^a Experimental data (extrapolated to $T = 0$ K) are provided in column 2 for comparison. Δ is the difference in percent between experimental and calculated values. ^b Reference 1. ^c Reference 16.

TABLE 3: Mulliken Population Analyses for the Valence Orbitals in the Structures Optimized with the Three Selected Basis Sets^a

AO		Si, [Ne]3s ² 3p ² no. valence e = 4			Mg, [Ne]3s ² no. valence e = 2	
		s	p	d	s	p
PP*	Z ^b	6.97				0.51
	Z _{OA} ^c	1.799	5.142	0.04	0.295	0.216
PP	Z ^b	7.52				0.23
	Z _{OA} ^c	1.897	5.63		0.236	
AE*	Z ^b	5.77				1.115
	Z _{OA} ^c	1.841	3.911	0.023	0.483	0.632

^a Z is the Mulliken net charge of atoms (in electrons). The detailed composition over the valence shells is listed as Z_{OA} (in electrons). ^b Z: number of electrons assigned to each atom. ^c Z_{OA}: number of electrons assigned to each atomic shell.

difference between two large quantities, namely, energies corresponding to $[\eta, 0, 0, 0, 0, 0]$ and $[\eta, \eta, 0, 0, 0, 0]$ strains. The other elastic constants are in better agreement with experimental results for the PP* and AE* basis sets. But the need for polarization orbitals is clearly demonstrated in Table 2, which shows the worsening in the results when these polarization orbitals are removed (compare the PP and the PP* columns in Table 3).

To study in detail the effect of the polarization orbitals on energy and on other properties, a series of calculations were carried out using various values of the exponents of the polarization AO's of the PP* basis or even removing one or both of them from it (the latter is the PP basis set listed in Table 1). The need for polarization functions on each center (d on Si, p on Mg) clearly appears from these calculations. This is not really surprising for the Mg(p) orbitals; the population analyses given in Table 3 and the energies in Table 1 show that these orbitals are more than simple "polarization" orbitals and that they are of utmost importance in order to describe properly the s-p hybridization on magnesium. From a careful comparative inspection of the values of elastic constants calculated with various exponents of the Mg(p) AO, it is found that the effect of this Mg(p) basis function is more important for the C_{11} and B coefficients, associated with compressions, than for the two others. The role of the d function on the Si center is even more selective though smaller in absolute magnitude. For symmetry reasons, the d polarization is important for those constants that are associated with torsions

and shears, namely, C_{12} and C_{44} , whereas it does not play any significant role for those that correspond to simple compressions (B and C_{11}). These observations can be paralleled with those extracted from molecular calculations on MX_2 compounds²³ where it was found that p polarization on alkaline earths are essential to describe stretching and d polarization on the ligand to describe bending.

It has been often noticed that first-principles calculations of moduli (and phonon frequencies) in the structure of the crystal fixed at the known experimental geometry usually give values closer to experimental values than calculations in the theoretically optimized structure. This was not found to be the case here. For instance, the ab initio optimized values of the lattice constant of Mg_2Si ($a = 6.506$ \AA with PP*, $a = 6.430$ \AA with AE*) differs only slightly from the experimental value ($a = 6.351$ \AA). Nevertheless, calculations of elastic constants carried out around the experimental structure lead to large overestimations with respect to those obtained around the energy-optimized structure. For instance, with the PP* basis set, the errors are +24% on B (72 GPa), +11% on C_{11} (163 GPa), +78% on C_{12} (27 GPa), and +42% on C_{44} (64.5 GPa).

C. Phonon Modes. The vibrational frequencies of the two transverse optical modes at the center of the Brillouin zone,²⁴ one Raman active (ν_R) and one IR active (ν_{IR}), were calculated within the frozen phonon approximation. The harmonic force constants were obtained from polynomial fits of E versus the displacements along the normal modes of vibration. The dynamic matrix was then diagonalized to extract the frequencies. With the PP* and AE* basis sets, the calculated frequencies differ by at most 10% from experimental values, which is the order of magnitude of what is usually expected in the HF approximation.¹⁰ The overestimation is much larger for the calculations with the PP basis set that lacks polarization orbitals.

D. Band Structure, Density of States, and Electronic Density Maps. Mg_2Si is known to be a small band gap semiconductor. For all tested basis sets, the energy band gap width between valence and conduction bands at the Γ point is about 3 times larger than the experimental value of 2.27 eV.¹ This overestimation reflects a well-known failure of the Hartree-Fock approximation for this property. Except for the value of the band gap, the main features of the band structure calculated with the three selected basis sets agree satisfactorily with those previously published on the basis of experimental measurements.^{3,4,8,25} Although every basis set can be expected to represent the ground-state quite accurately, the excited levels, which correspond to virtual orbitals in the HF process, are more dependent on the basis set. As an example, the AE* calculated band structure of Mg_2Si is drawn in Figure 2.

Figure 3 represents the electronic density of states of Mg_2Si and projections of this density onto the atomic shells for the AE* calculations. The valence band is split into two subbands. The lowest one is mainly 3s(Si) with a negligible contribution of the 3s and 3p levels of Mg. The highest one is essentially made of 3p(Si), and there also, the contribution of the magnesium orbitals is negligible. Thus, this analysis of the AE* density of states is in favor of an ionic character for the Mg-Si bond in Mg_2Si . This is confirmed to a certain extent by the electron density map of Figure 4. This map shows that the valence electrons are mainly around the Si atoms, although there is an indication of a weak covalency between Si and Mg. The admixture of covalency into the Mg-Si bond is more obvious when looking at the AE* Mulliken populations (Table 3). From this point of view, the structure of the Mg-Si bond in terms of net charges is roughly $\text{Mg}^{0.9+}\text{Si}^{1.8-}$ (compared to the fully ionic formula $\text{Mg}^{2+}\text{Si}^{4-}$). It is noted that the Mulliken populations

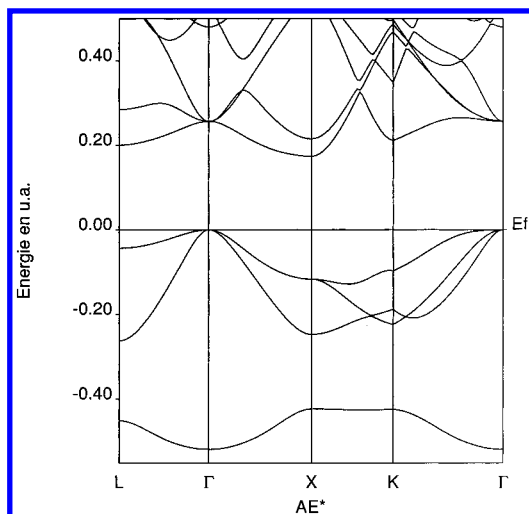


Figure 2. Valence electronic band structure of Mg₂Si obtained with the AE* basis set.

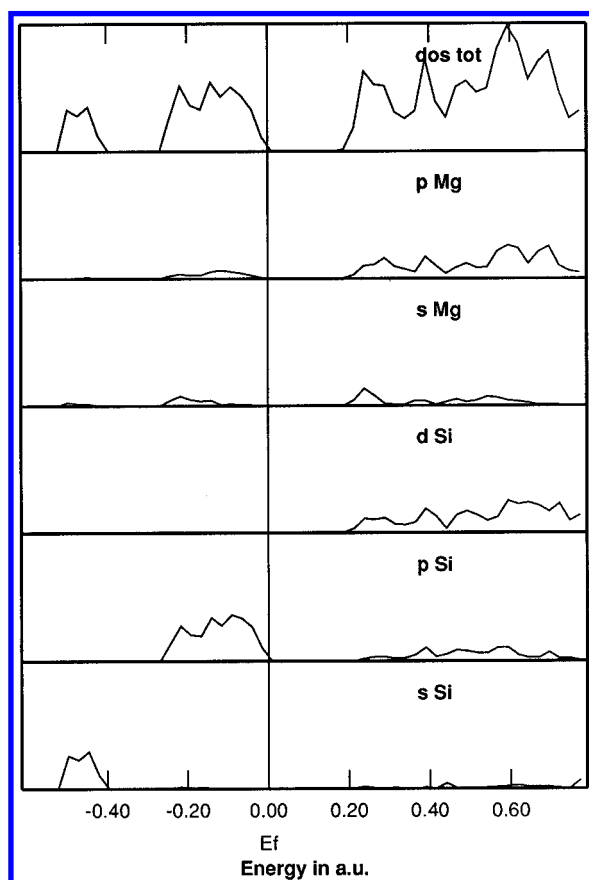


Figure 3. Atomic orbital projections of the density of states obtained with the AE* basis set for the valence orbitals of Mg₂Si. The atomic orbital contributions have been obtained using a Mulliken partition scheme.

taken from PP* calculations lead to a markedly more ionic nature for the Mg–Si bond. This is obviously a consequence of the freezing of inner shells in calculations using pseudopotentials.

Finally, the mixed covalent–ionic character for the Mg–Si bond found in the present all-electron calculations of Mg₂Si brings an intermediate insight that softens the extreme points of view that can be found in the literature relating to the nature of the bonding in Mg₂Si. On one hand, this bonding is less ionic than that arising from the DFT calculations of D. Wood and A. Zinger⁹ as well as from the discussion of the XPS experimental results by J. Tejeda and M. Cardona.³ But on the

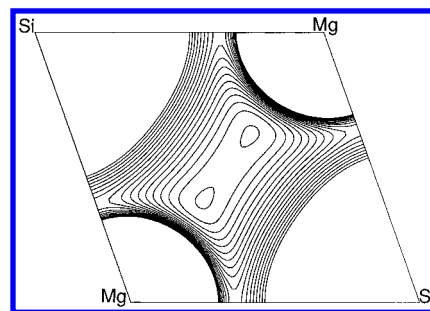


Figure 4. Electron density maps on the (110) plane through Mg and Si atoms. The curves closest to atomic centers correspond to a density of 0.03 bohr⁻³ (maximum density value plotted, which eliminates visualization of the cores). The separation between isodensity curves is 0.001 e bohr⁻³.

other hand, it certainly does not have the covalent character claimed by A. J. Bevolo and H. R. Shanks²⁵ on the basis of their Auger spectroscopy data and speculated by Eldridge et al. from a comparison of the separations in the crystal with ionic, metallic, and covalent radii of atoms.²⁶

4. Conclusion

These ab initio SCF-HF-LCAO calculations carried out with several bases of unequal quality have confirmed the necessity of using and optimizing flexible and polarized sets of atomic functions, especially when one deals with properties directly related to the electronic potential energy surface of the crystal. Whereas static properties such as lattice constants, ground-state band structures, or electronic charge density distributions are satisfactorily described whatever the basis set, phonon frequencies and elastic constant calculations do require refined basis sets. It has been pointed out that the polarization functions play an important and selective role for these latter properties. It has been found that the use of Durand's and Barthelat's pseudopotentials to represent the cores is satisfactory for the calculations of the structure and elastic constants but it is less satisfactory for charge densities.

The calculations have shown that the Mg–Si bonding in magnesium silicide is between covalent and ionic (see Table 3). This mixed character explains the controversy that arose from interpretations of various experimental data^{3,25} relating to the ionicity of the compound.

In the course of the calculations of the elastic constants associated with shears (C_{44}), it has been found that very small relaxations within the unit cell driven by external strains are responsible for a significant part of the macroscopic value. This possibility of linking the very microscopic level to macroscopic constants makes ab initio calculations a powerful tool for interpreting at a quantitative level the manifold of phenomena encountered in condensed matter physics. This by itself justifies the efforts to improve these heavy ab initio methods in view of understanding the structures of solids as well as simulating their dynamical properties.

Acknowledgment. The "Centre d'Etudes et de Recherches Lasers et Applications" (CERLA) is supported by the Ministère chargé de la Recherche, the Région Nord/Pas de Calais, and the Fonds Européen de Développement Economique des Régions. The calculations have been partly carried out at the national computer center IDRIS in Orsay. We acknowledge the CNRS (Mathematical and Physical Science Department) and the Ministère chargé de la Recherche for a generous allocation of computer time (Contract 960244). We are grateful to Dr. Ales Zupan for providing graphical software adapted to CRYSTAL-92 data and the referee for useful comments.

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