

Phase transition and optical properties of CaCl_2 under high pressure by *ab initio* pseudopotential plane-wave calculations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 425225

(<http://iopscience.iop.org/0953-8984/19/42/425225>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 06:14

Please note that [terms and conditions apply](#).

Phase transition and optical properties of CaCl_2 under high pressure by *ab initio* pseudopotential plane-wave calculations

Y H Liu, Y M Ma, Z He, T Cui¹, B B Liu and G T Zou

National Lab of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

E-mail: cuitian@jlu.edu.cn

Received 3 August 2007

Published 18 September 2007

Online at stacks.iop.org/JPhysCM/19/425225

Abstract

We present a detailed investigation of CaCl_2 under high pressure in CaCl_2 ($Pnmm$, $Z = 2$) and $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$) phases, respectively. Theoretical calculations are performed by using the *ab initio* pseudopotential plane-wave method based on the density functional method. We estimate the transition pressure between the two phases by the crossing point of their enthalpies, which are equivalent to the Gibbs free energy at zero temperature, after optimizing the structures under high pressure. Our results show that the transition happens at about 2.9 GPa, which is in agreement with the experimental data. We calculate the structural parameters, charge transfers, bond structures, density of states and optical properties. The calculated results show that there are no charge transfers in CaCl_2 structure under high pressure. It is found that the transitions from the Cl 3p to Ca 4s and Cl 3s to Ca 3p orbitals contribute mainly to the dielectric function. The optical properties of CaCl_2 ($Pnmm$, $Z = 2$) do not vary much under pressure. However, some of the dispersion curves of optical constants in the $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$) phase are changed significantly under pressure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The high-pressure polymorphism in AX_2 compounds has been extensively studied, and a clear picture is beginning to emerge due to *in situ* measurements [1–5]. The cotunnite structure is the final known step in the phase-transition sequence of the AX_2 compounds investigated to date. The structure of AX_2 compounds can be divided into four main groups based upon the constituent cation-centered anion polyhedra: the quartz group, the rutile group, the fluorite group, and the countinite group.

¹ Author to whom any correspondence should be addressed.

Rutile-type ($P42/mnm$, $Z = 2$, coordination number = 6) dioxides undergo one or more transitions towards a cotunnite structure ($PbCl_2$) ($Pnam$, $Z = 4$, coordination number = 9) via either the baddeleyite ($P21/c$, $Z = 4$, coordination number = 7) or the cubic $Pa\bar{3}$ ($Z = 4$, coordination number = 8) structure. This intermediate baddeleyite structure is only found in compounds in which the cation has an empty d shell [1, 6], for example, TiO_2 ($Ti^{4+}:(Ar)3d^0$) under high pressure, ZrO_2 ($Zr^{4+}:(Kr)4d^0$) and HfO_2 ($Hf^{2+}:(Xe)5d^0$) at ambient pressure.

Lower coordination numbers (coordination number = 6) are found in $CaCl_2$ and $CaBr_2$ with $CaCl_2$ -type structure and CaI_2 with a layered structure. The symmetry of the structure is orthorhombic, space group $Pnmm$ ($Z = 2$), which is a direct subgroup of $P42/mnm$. The transition sequence in $CaCl_2$ is of particular interest as it should transform to the cotunnite $PbCl_2$ structure via the EuI_2 baddeleyite structure ($P21/c$, $Z = 4$, coordination number = 7) rather than the cubic $Pa\bar{3}$ ($Z = 4$, coordination number = 8) structure, because the calcium cation Ca^{2+} has the configuration $(Ar) 3d^0$ as Ti^{4+} . In addition, the phase sequence with increasing pressure for $CaCl_2$ is of further interest as silica adopts the $CaCl_2$ -type structure under very high pressure.

In the present paper, we report the optical properties of the $CaCl_2$ ($Pnmm$, $Z = 2$) phase and the α - PbO_2 ($Pbcn$, $Z = 4$) phase under ambient and structural phase transition pressures, respectively. We estimate the transition pressure at about 2.9 GPa between the two phases by the crossing point of their enthalpies, after optimizing the structures under high pressure. The Mulliken population shows that there is no charge transfer under phase transition pressure. Then, we discuss the optical properties, including the dielectric function, absorption, refractive index, electron energy loss function and reflectivity. We also calculate the electronic structures, of which the optical properties depend on the transitions determined by the energy bands.

2. Computational details

We focus on the orthorhombic $CaCl_2$ crystal with a six-atom unit cell using the *ab initio* pseudopotential density functional theory. All the possible structures under pressure are optimized by the BFGS algorithm proposed by Broyden, Fletcher, Goldfarb and Shannon [7], which provides a fast way of finding the lowest energy structure. Norm-conserving pseudopotentials for Ca and Cl are generated using the scheme by Troullier and Martins [8, 9]. The local-density approximation (LDA) [10] is used to describe the exchange and correlation effects. Convergence tests give an energy cut-off of 550 eV and a $4 \times 4 \times 6$ Monkhorst–Pack k -point mesh is used in the electronic Brillouin zone integration for all structures. All calculations are completed by the CASTEP code [11].

3. Results

Calcium dichloride ($CaCl_2$) is a ferroelastic material, which, at ambient pressure, exists in two phases: a high temperature (above $T_c = 491$ K) tetragonal (rutile-type, space group $P42/mnm$, $Z = 2$) and a low-temperature orthorhombic (space group $Pnmm$, $Z = 2$) phase. The ferroelastic instability between the tetragonal and low-temperature orthorhombic phases was discussed in [12–14]. Our studies are from the orthorhombic phase, which is stable at ambient conditions. The $CaCl_2$ ($Pnmm$) phase undergoes a phase transition sequence which is unique among the AX_2 compounds [15–17]. In a narrow pressure range $CaCl_2$ crystallizes in five different phases with $CaCl_2$, α - PbO_2 , EuI_2 , SrI_2 , and $PbCl_2$ -type structures [18]. No other AX_2 compound undergoes such a large variety of transitions [19, 20]. The coordination number increases from six in $CaCl_2$ and α - PbO_2 structures to seven in EuI_2 and SrI_2 structures and finally to nine in cotunnite structure.

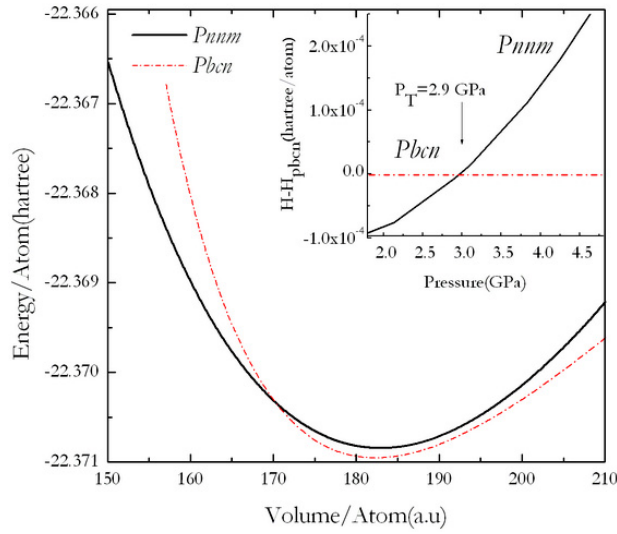


Figure 1. The computed total energy versus volume in the two structures, for CaCl_2 ($Pnmm$) and $\alpha\text{-PbO}_2$ ($Pbcn$). Inset: enthalpy ($E + PV$) versus pressure P for the CaCl_2 and $\alpha\text{-PbO}_2$ phases.

Table 1. Structural parameters and bulk modulus of the fully relaxed orthorhombic phase of CaCl_2 compared with the experimental values extrapolated to 0 K [12–14]. The x and y atomic coordinates for Cl atoms are given in lattice units.

	a_0 (Å)	b_0 (Å)	c_0 (Å)	v	x (Cl)	y (Cl)	B_0 (GPa)
Present (LDA)	6.337	6.181	4.171	163.399	0.345	0.258	30.08
Present (GGA)	6.433	6.592	4.283	181.623	0.328	0.280	
Expt. [14]	6.446	6.167	4.137	164.456	0.325	0.275	
LDA [12]	6.429	6.054	4.088	159.109	0.347	0.255	31
GGA [13]	6.474	6.386	4.162	171.584	0.316	0.291	

The equilibrium lattice parameters are determined by fitting the total energies as a function of volume to the Murnaghan equation of state [21]. The equilibrium lattice parameters together with another pseudopotential plane wave calculation [12, 13] and the experimental data [14] are listed in table 1. The lattice parameters which we calculated in the LDA are in excellent agreement with the experimental results. The bulk modulus calculated from the ambient pressure data of CaCl_2 is 30.08 GPa and is in reasonable agreement with the other theoretical results of 31 GPa [12]. We also present the Cl coordinates [X^{Cl} , Y^{Cl}] in table 1. The positions of cations are fixed by crystal symmetry. Our results suggest that norm-conserving pseudopotentials and the LDA approximation should be used for high pressure studies.

The total energy as a function of volume is plotted in figure 1 for CaCl_2 ($Pnmm$) and $\alpha\text{-PbO}_2$ ($Pbcn$) phases. The enthalpy $H(P) = E + PV$, as a function of pressure for CaCl_2 and $\alpha\text{-PbO}_2$ phases, is shown in the inset of figure 1. The transition pressure is estimated from the cross-points ($P = 2.9$ GPa) of the enthalpy curves. Above 2.9 GPa, the $\alpha\text{-PbO}_2$ phase becomes energetically more favorable. The transition pressure of 2.9 GPa is in excellent agreement with the measurement (3.0 GPa) [18].

During the phase transition between the CaCl_2 ($Pnmm$) and $\alpha\text{-PbO}_2$ ($Pbcn$) phases, the coordination number remains six. For understanding the phase transition mechanism, we analyze the atomic charges, chemical bond lengths, and bond population by means of the

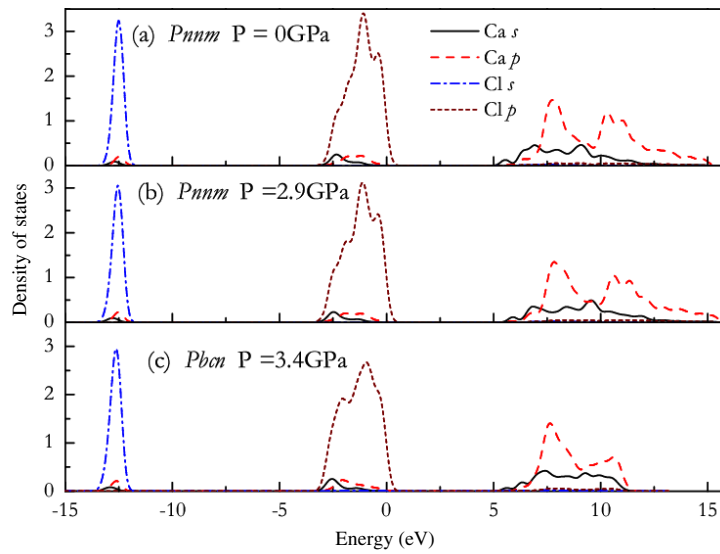


Figure 2. Density of states (DOS) for Cl 3s, 3p and Ca 3s, 3p, 4s under ambient pressure and 2.9 GPa, and the α -PbO₂ (*Pbcn*) structure under 3.4 GPa.

Mulliken analysis [22, 23]. The Mulliken charges are $-0.66e$ for the Cl atom and $1.32e$ for the Ca atom in CaCl₂-type phase under ambient and at high pressure of 2.9 GPa, respectively. There is no charge transfer induced by pressure observed in this high pressure range. The bond population of Ca–Cl decreases from 0.12 to 0.1 as the pressure increases from 0 to 2.9 GPa, indicating a weaker covalency induced by pressure. Even though the coordination number is not changed under pressure, it shows a trend of bonding from covalency to ionicity.

The density of states (DOS) of the CaCl₂ (*Pnmm*) phase under ambient and phase transition pressures (2.9 GPa) and the α -PbO₂ (*Pbcn*) phase under 3.4 GPa is plotted in figure 2. The results show that the 3s and 3p orbitals of Cl mostly contribute to the occupied bands near the Fermi level. We find that when CaCl₂ (*Pnmm*) is compressed, the peak of the DOS in the valence bands has a slight tendency to shift to lower energy. For instance, the peak of the Cl 3s orbital is shifted from -12.518 to -12.561 eV and the peak of the Cl 3p orbital is shifted from -1.058 to -1.107 eV, respectively. In the α -PbO₂ (*Pbcn*) phase, the peak of the Cl 3p orbital is shifted to smaller energies than those in the CaCl₂ (*Pnmm*) phase, at -12.64 eV. The peak of the Cl 3p orbital is shifted to higher energy than that in the CaCl₂ (*Pnmm*) phase at -0.982 eV. Moreover, the peaks of the Cl 3s and Cl 3p are slightly narrowed.

The optical properties in the two phases have been rarely reported so far. These properties are also of great importance in giving insight into the fundamental physical properties and potential applications. The dielectric function, the absorption coefficient, the refractive index, the electron energy-loss spectrum and the reflectivity have been calculated in this paper. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function could be calculated from the momentum matrix elements between the occupied and unoccupied wavefunctions within the selection rules, and the real part $\varepsilon_1(\omega)$ of the dielectric function can be evaluated from the imaginary part $\varepsilon_2(\omega)$ by the Kramer–Kronig relationship [24]. All the other optical constants can be derived from $\varepsilon_2(\omega)$ and $\varepsilon_1(\omega)$, such as the reflectivity $R(\omega)$, the electron energy-loss spectrum $L(\omega)$, the absorption coefficient $\alpha(\omega)$ and the refractive index $n(\omega)$.

We plot the dielectric functions of the CaCl₂ phase under ambient and phase transition pressure of 2.9 GPa, and the α -PbO₂ phase under 3.4 GPa in figure 3. The line shape of the

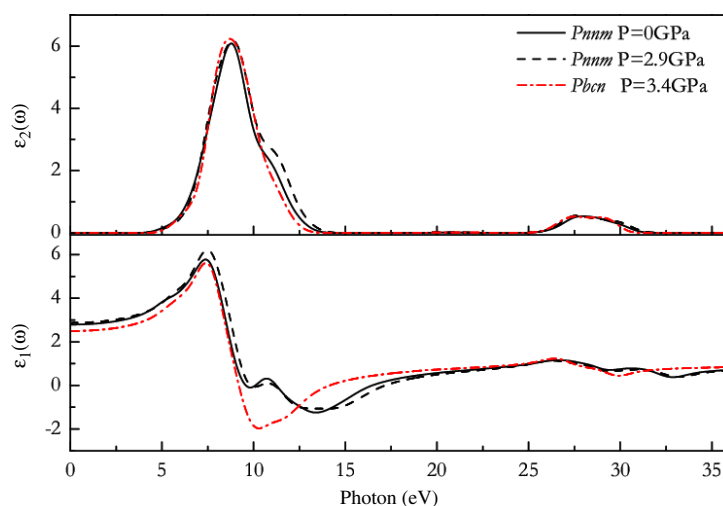


Figure 3. The dielectric function of the imaginary part $\varepsilon_2(\omega)$ and the real part $\varepsilon_1(\omega)$ for the CaCl_2 ($Pnmm$) phase under 0 and 2.9 GPa, and the $\alpha\text{-PbO}_2$ ($Pbcn$) phase under 3.4 GPa.

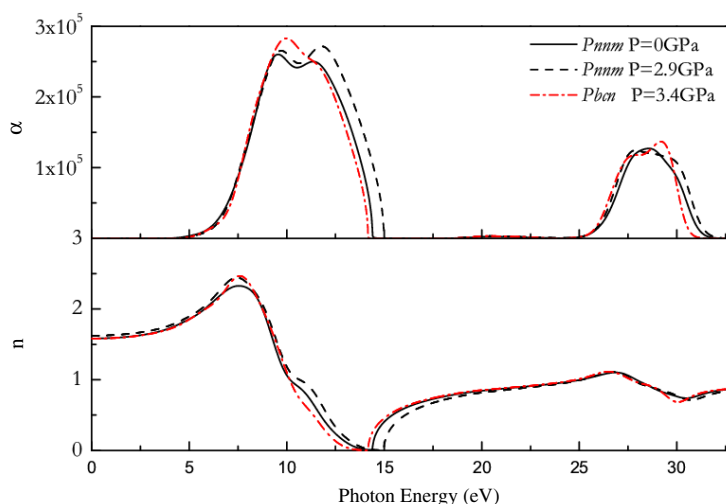


Figure 4. The absorption coefficient $\alpha(\omega)$ and the refractive index $n(\omega)$ of CaCl_2 under 0 and 2.9 GPa, and the $\alpha\text{-PbO}_2$ phase under 3.4 GPa.

imaginary part of the dielectric function $\varepsilon_2(\omega)$ is almost unchanged in these phases. With the increase of pressure, the peaks of the CaCl_2 and the $\alpha\text{-PbO}_2$ phases all increase while shifting to the low energy region (red shift). By comparing with the density of states, we find that the peak at about 10 eV mainly comes from the electron transition from the Cl 3s to Ca 3p orbitals shown in figure 2. The transition from the Cl 3p to Ca 4s orbitals contributes to the peak at about 27 eV. The real part of the dielectric function $\varepsilon_1(\omega)$ is also plotted. The $\varepsilon_1(0)$ in the CaCl_2 phase are 2.79 and 2.87 at ambient pressure and 2.9 GPa, respectively, which is bigger than the 2.49 for the $\alpha\text{-PbO}_2$ phase under 3.4 GPa.

The absorption coefficient $\alpha(\omega)$ and the refractive index $n(\omega)$ of CaCl_2 and $\alpha\text{-PbO}_2$ phases are presented in figure 4. The absorption edges of the CaCl_2 phase under 0 and 2.9 GPa are

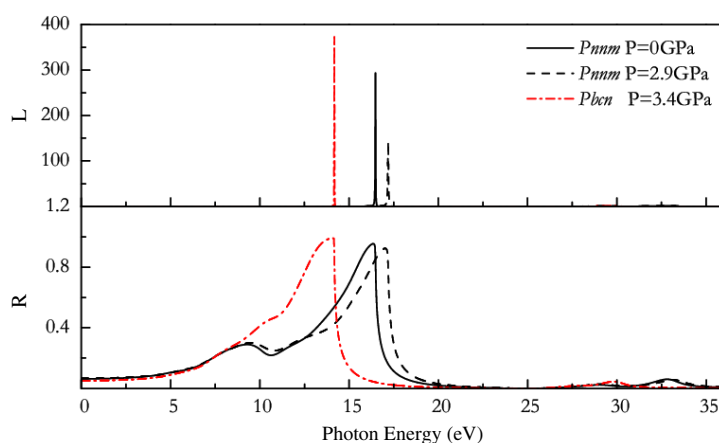


Figure 5. The electron energy-loss function $L(\omega)$ and the reflectivity $R(\omega)$ of CaCl_2 under 0 and 2.9 GPa, and the $\alpha\text{-PbO}_2$ phase under 3.4 GPa.

similar to the $\alpha\text{-PbO}_2$ phase under 3.4 GPa. Both of the phases have no absorption in the low energy regime from 0 to 5 eV, showing that they are all transparent, because such a range of phonon energy is just within the forbidden band. There are two main peaks in the CaCl_2 phase under ambient pressure, located from 0 to 14.5 eV and 25 to 32 eV, respectively. These two peaks are located at 0–15 eV and 25–32 eV at 2.9 GPa, showing that there is no obvious change caused by pressure. In the $\alpha\text{-PbO}_2$ phase, the two peaks are all smaller than those in the CaCl_2 phase. The refractivity of the $\alpha\text{-PbO}_2$ phase is similar to that of the CaCl_2 phase. In the energy range from 0 to 7.5 eV, they all have normal dispersions. But in the photon energy ranges from 7.5 to 14 eV and 7.5 to 11 eV, the two structures show anomalous dispersions, respectively.

We plot the electron energy-loss spectrum $L(\omega)$ and the reflectivity $R(\omega)$ of the CaCl_2 phase under ambient and phase transition pressures, and the $\alpha\text{-PbO}_2$ phase under 3.4 GPa in figure 5. $L(\omega)$ can describe the energy loss of a fast electron traversing in a material. The peaks in the $L(\omega)$ spectra represent the characteristic associated with the plasma resonance, and the corresponding frequency is the so-called plasma frequency determined by $\omega_p^2 = Ne^2/m$, where N is the density of the valence electrons of the sample. Above the plasma frequency the material exhibits the dielectric behavior ($\epsilon_1(\omega) > 0$) while below it the material behaves as metallic ($\epsilon_1(\omega) < 0$). That is to say, the positions of peaks in the $L(\omega)$ spectra also indicate the point of transition from the metallic property to the dielectric property for a material. In addition, the peaks of $L(\omega)$ also corresponds to the trailing edges in the reflection spectra. The peak of $L(\omega)$ for the CaCl_2 phase is located at 16.48 eV at ambient pressure and has a blue-shift to 17.16 eV at 2.9 GPa, where the reflectivity is also sharply reduced, respectively. From figure 5, we also see that the peak of $L(\omega)$ for the $\alpha\text{-PbO}_2$ phase at 14.2 eV is smaller than that of the CaCl_2 phase.

4. Conclusion

The phase transition of CaCl_2 from CaCl_2 phase to $\alpha\text{-PbO}_2$ phase, the Mulliken population and the optical properties have been investigated by the *ab initio* norm-conserving pseudopotential density functional method in detail. The transition between the CaCl_2 ($Pnmm$, $Z = 2$) and $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$) structures happens at 2.9 GPa, which is in agreement with the measurement. Mulliken analysis shows that the two structures are similar and there is no

significant charge transfer induced by pressure in the CaCl_2 phase. The optical properties of CaCl_2 ($Pnmm$, $Z = 2$) under the ambient and the structural phase transition pressure and the $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$) structure at 3.4 GPa are investigated, respectively. The dielectric function and the optical properties such as the absorption coefficient $\alpha(\omega)$, the refractive index $n(\omega)$, the electron energy-loss spectrum $L(\omega)$ and the reflectivity $R(\omega)$ are presented. The results show that the transitions from the Cl 3p to Ca 4s and Cl 3s to Ca 3p orbitals contribute mainly to the peaks of the dielectric function. The optical properties of CaCl_2 ($Pnmm$, $Z = 2$) do not vary much under pressure. However, the dispersion curves of $L(\omega)$ and $R(\omega)$ in the $\alpha\text{-PbO}_2$ phase are changed significantly caused by pressure. Our results are helpful for a better understanding of the phase transitions in AX_2 compounds.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under grant nos 10574053, 10674053 and 10664005, 2004 Program for New Century Excellent Talents in University and 2003 Excellent Young Teachers Program of Ministry of Education of China, and National Basic Research Program of China, grant nos 2005CB724400 and 2001CB711201, and the Cultivation Fund of the Key Scientific and Technical Innovation Project (grant no 2004-295).

References

- [1] Léger J M and Haines J 1997 *Eur. J. Solid State Inorg. Chem.* **34** 785
- [2] Léger J M, Haines J and Atouf A 1995 *Phys. Rev. B* **51** 3902
- [3] Léger J M, Haines J, Atouf A and Schulte O 1995 *Phys. Rev. B* **52** 13247
- [4] Sato H, Endo S, Sugiyama M, Kikegawa T, Shimomura O and Kusaba K 1991 *Science* **251** 786
- [5] Haines J, Léger J M and Schulte O 1996 *Science* **271** 629
- [6] Jaffe J E, Bachorz R A and Gutowski M 2005 *Phys. Rev. B* **72** 144107
- [7] Fischer T H and Almlöf J 1992 *J. Phys. Chem.* **96** 9768
- [8] Lin J S, Qteish A, Payne M C and Heine V 1993 *Phys. Rev. B* **47** 4174
- [9] Louie S G, Froyen S and Cohen M L 1982 *Phys. Rev. B* **26** 1738
- [10] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [11] Segall M, Lindan P, Probert M, Pickard C, Hasnip P, Clark S and Payne M 2002 *J. Phys.: Condens. Matter* **14** 2717
- [12] Válgoma J A, Perez-Mato J M and Garcia A 2002 *Phys. Rev. B* **65** 134104
- [13] Łazewski J, Jochym P T, Piekarczyk P and Parlinski K 2004 *Phys. Rev. B* **70** 104109
- [14] Unruh H G, Muhlenberg D and Hahn Ch 1992 *Z. Phys. B* **86** 133
- [15] Łodziana Z, Parlinski K and Hafner J 2001 *Phys. Rev. B* **63** 104106
- [16] Kang J, Lee E C and Chang K J 2003 *Phys. Rev. B* **68** 054106
- [17] Haines J and Léger J M 1997 *Phys. Rev. B* **55** 11144
- [18] Léger J M, Haines J and Danneels C 2002 *J. Phys. Chem. Solids* **59** 1199
- [19] Haines J, Léger J M and Schulte O 1996 *J. Phys.: Condens. Matter* **8** 1631
- [20] Narasimhan S and Gironcoli S 2002 *Phys. Rev. B* **65** 064302
- [21] Birch F 1947 *Phys. Rev.* **71** 809
- [22] Segall M D, Pickard C J, Shah R and Payne M C 1996 *Mol. Phys.* **89** 571
- [23] Segall M D, Shah R, Pickard C J and Payne M C 1996 *Phys. Rev. B* **54** 16317
- [24] Saha S and Sinha T P 2000 *Phys. Rev. B* **62** 8828