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FOR ADVANCED STUDIES

Thesis submitted for the degree
of
MAGISTER PHILOSOPHIÆ

HIGH-PRESSURE STUDIES IN SOME ALKALI HALIDES

CANDIDATE:
Edmondo De Salvo

SUPERVISOR:
Prof. S. Baroni

Academic year 1986/1987

TRIESTE

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INTERNAZIONALE
SUPERIORE
DI STUDI AVANZATI
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INTRODUCTION

In the course of the last years a renewed interest has been devoted to the study of alkali halides under high pressure. The interest in the high-pressure properties of matter is wide and common to several areas of physics, such as solid-state physics, geophysics and astrophysics. From a fundamental point of view, it is interesting to investigate the behaviour of the electronic states in such extreme conditions, also in connection with the problem of the band-overlap metallization transition and structural distortions. In this framework, many of the alkali halides are very interesting candidates for the study of these problems, because their moderate compressibility allows to explore experimentally such phase transitions (see e.g.: Williams,1986). Furthermore, their simple microscopic structure simplifies the interpretation of the experimental measures, thus giving the opportunity to get partial insight about more complicate systems .

In this thesis the structural properties of some alkali halides are studied both at zero pressure and high applied pressures. This is done either by the application of a Born-Mayer like semiempirical model and by *ab-initio* pseudopotential calculations within the Local Density Functional (LDF) formalism.

The basic motivations to undertake this research are connected to the attempt of better understanding the peculiar structural properties observed in cesium halides and, more generally, in alkali halides at very high pressure ($\sim$ 1 $Mbar$). All these compounds undergo structural phase transitions under the action of an applied pressure. In particular, cesium iodide exhibits spontaneous lowering of the crystalline symmetry. Starting from a simple cubic lattice, this system assumes first a tetragonal structure and subsequently a more distorted one, which has not yet found an exhaustive explanation. Analogous phenomena has been detected in both cesium chloride and cesium bromide.

In particular, the spontaneous symmetry lowering, observed in cesium halides [Asaumi 1984, Knittle 1985, Brister 1985], is a formidable problem for *ab-initio* theoretical studies. Up to now, only the mechanism for the cubic to tetragonal transition has been explained, by both semiempirical [Vohra, Duclos 1985] and first-principle [Christensen 1985; Baroni 1987] calculations; on the contrary, the further structural distortion has not yet found any theoretical explanation. Finally, it would be interesting to understand if such transitions are common to all ionic crystals, as someone suppose [Vohra, Duclos 1985], or else they are a peculiar characteristic for cesium halides [Asaumi 1984, Knittle 1985, Brister 1985].

The outline of this thesis is the following. In chapter 1 the experimental aspects are discussed: a brief review of the instrumentation and their applications are reported in the first two paragraphs; another paragraph is devoted to the alkali halides, their structural behaviour, and recent experimental studies. Chapter 2 contains the theoretical results obtained in the course of the present research and a review of those reported in literature. The chapter is divided into three paragraphs: in the first the Born model is discussed, then we analyze previous results and present new calculations for cesium halides and rubidium bromide; the second paragraph contains a review of some techniques adopted to study the ionic crystals; finally, in the third paragraph the *ab-initio* pseudopotential technique within LDF formalism is described and our results obtained by its application are presented and discussed.

CHAPTER 1

The Diamond-Anvil High-Pressure Cell and its Applications

A) Instruments

The development of the experimental investigations about the properties of matter at very high pressures dates back to the beginning of this century. P.W. Bridgman of Harvard University pioneered these studies for more than half a century until his death in 1961. Not only did Bridgman study a remarkable number of elements and compounds under high pressure but also he invented every technique he worked with. The present anvil cells differ little from Bridgman's one: the developments have pertained the introduction of diamonds to construct the anvils, the employment of new materials for the calibration of the pressure, and the adoption of optical techniques to investigate the modification in the sample.

The essential configuration of a Diamond Anvil Cell (DAC) is shown in fig.1. The basic principle of the DAC is simple. A sample placed between the flat parallel faces of two opposed diamond anvils is subject to pressure when a force pushes the two opposed anvils together. However, variations in the DAC arise from different ways in which the forces generating and the anvil alignment mechanisms can be designed. Other differences are due to the temperature range in which the DAC is employed. Presently, applications from 2 to few thousands Kelvin degrees are available.

In the DAC illustrated in fig.1 we distinguish a metallic gasket and the presence of a pressure medium, these two elements were introduced by Bridgman to obtain an hydrostatic pressure on the sample (for a wide experimental review see: [Jayaraman]).

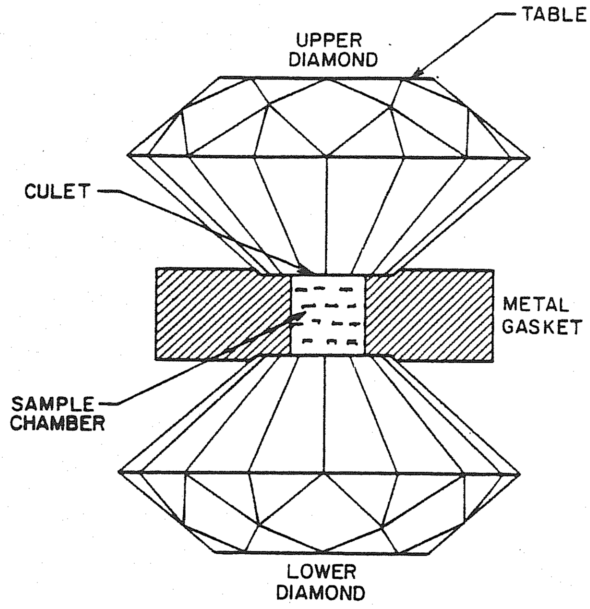


fig.1 : Schematic design of a Diamond Anvil Cell.

B) Applications: A Brief Review

The study of the matter with the DAC is fundamental in several areas of physics, such as solid-state physics and also for geophysics and astrophysics. A complete review of all the experiments reported in the literature is out of our scopes, however it's interesting to report some meaningful examples. The present instrumentation permit to study previously unaccessible portions of the Pressure-Volume-Temperature phase diagrams of elements and compounds. Among the solids, large attention has been devoted to alkali halides and semiconducting compounds. The topics of these studies are the vibrational properties (phonons), the structural phase transitions and the metallization transition in insulators and semiconductors. The case of the silicon is one of teh most interesting, because its high-pressure phases are all superconductors. The (Sh)-phase exhibits a maximum $T_c = 8.2\ K$ at 15 Gpa, and the β-Sn phase for $T_c = 6.3\ K$ at 15 Gpa (see: Jayaraman and references therein).

Also molecular crystals, such as H_2, D_2, and noble gas solids, have been studied by the DAC's. For hydrogen and deuterium the interest is connected to the attempt to confirm the strange properties that theoretical researches have predicted (superfluid and superconducting phases). Furthermore, as they are the constitutive elements of some stellar bodies, it is interesting to know their features at high temperature and pressure.

Several studies have been devoted to iron and metal oxides at high temperature, because they form the deep layers of the earth's mantle, and are important to understand the dynamics of the planets.

The DAC has been a important tool in establishing pressure-induced valence changes due to $4f$ electron delocalization in systems containing Sm, Eu, Yb, and Tm by high-pressure *x-ray* diffraction studies [Croft 1980; Werner 1981]. These transitions are isostructural and 1^{th}-order in some compounds (SmS, Sm_4Bi_3), while are continous, producing anomalous compression behaviour in Yb-compounds. For actinides, theoretical calculations [Skriver 1980; Johansson 1981] predict that compressed Am should exhibit a $5f$-delocalization transition near 100 Kbar. $X-ray$ diffraction investigations in the DAC [Akella 1980] have indicated a transition at 110 Kbar from fcc to AmIII, and yet another transition to AmIV at 150 Kbar. However, there is disagreement as to the identity of phases III and IV, and hence the fcc-AmIII volume change is not yet known.

Alkali Halides

A) Zero-Pressure Properties

The set of materials analyzed in this thesis is that of alkali halides, with a particular attention to their structural behaviour under high pressure. At low pressure, all these material are insulators and are characterized by an ionic bond. Alkali halides at zero pressure exhibit a cubic type structure: cesium salts (CsCl, CsBr, CsI) crystallize in the cesium chloride structure (B1) (fig.2a), which is formed by a simple cubic lattice with a basis consisting of a cesium ion at the origin and an halogen ion at the cube centre $(a/2)(\mathbf{1},\mathbf{1},\mathbf{1})$; all the others assume the rocksalt structure (B2) (fib.2b).

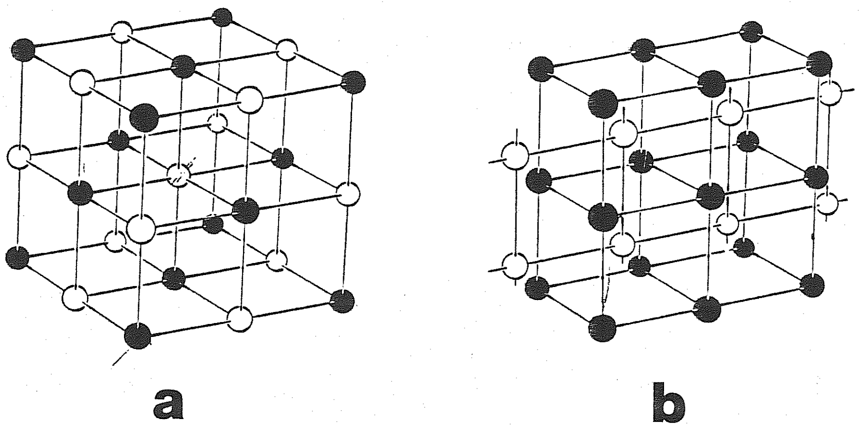


fig.2 : (a) Rocksalt structure, (b) Cesium chloride structure.

In these solids we have a charge transfer from the metallic atom to the halogen, which allows to both them assuming a very stable electronic configuration (rare gases electronic configuration). Consequently we have: a strong localization of the charge in the neighbourhood of the nuclei with spherical symmetry (see fig.3 for a typical electronic distribution in alkali halides), and the formation of a large energy gap between the upper filled band and the lower empty band.

B) High-Pressure Properties

The pressure induced insulator-metal transition is one of the most interesting phenomena occurring at high pressure. Many authors have reported such

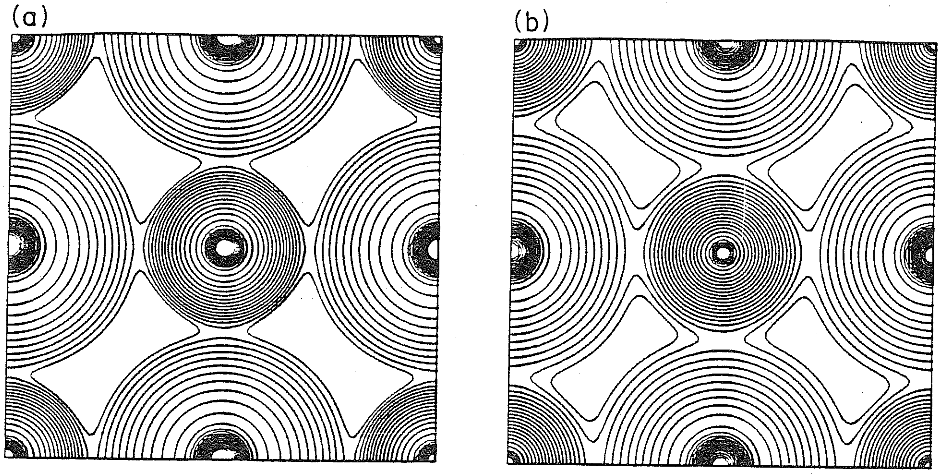


fig.3 : Experimental (a) and theoretical (b) charge density contours in a (100) plane for NaCl [*H.Jansen et al.: Phys.Rev.B***33**,8629(1986)]

a metallization process for semiconducting elements and compounds (see, e.g.: Phillips,1971). In principle, all the materials have to perform such a transition, due to the overlap of the upper valence band and the lower conduction band. However, large gap materials, as e.g. insulators, are no easily compressible at little volumes, because, due to the Pauli principle, the overlap between closed-shell atomic charges costs much energy.

Among all the alkali halides, the metallization transition has been observed only in cesium iodide (see e.g.: Williams 1986), which is the most soft of them.

Above we have briefly described the zero-pressure structure of alkali halides. The rubidium and potassium halides are subjected to the transition from the rocksalt to the cesium chloride structure at moderate pressures, of the order of 5 Kbar for the firsts and 20 Kbar for the seconds [Cohen A.J.,1975; Demarest, 1978; Asaumi, 1983; Heinz, 1984]. Also for NaCl and NaF such a transition has been observed but at higher pressures, of the order of 30 Kbar [Sato-Sorensen, 1983; Yagi, 1983]. Apart from the exceptions of NaBr and NaI, which assume a distorted rocksalt structure [Yagi (1983)], we may conclude that the cesium chloride arrangement is generally the stable phase for the alkali halides at moderately high pressure.

B.1) Cesium Halides (CsI, CsBr, CsCl)

B.1.1) Cesium Iodide

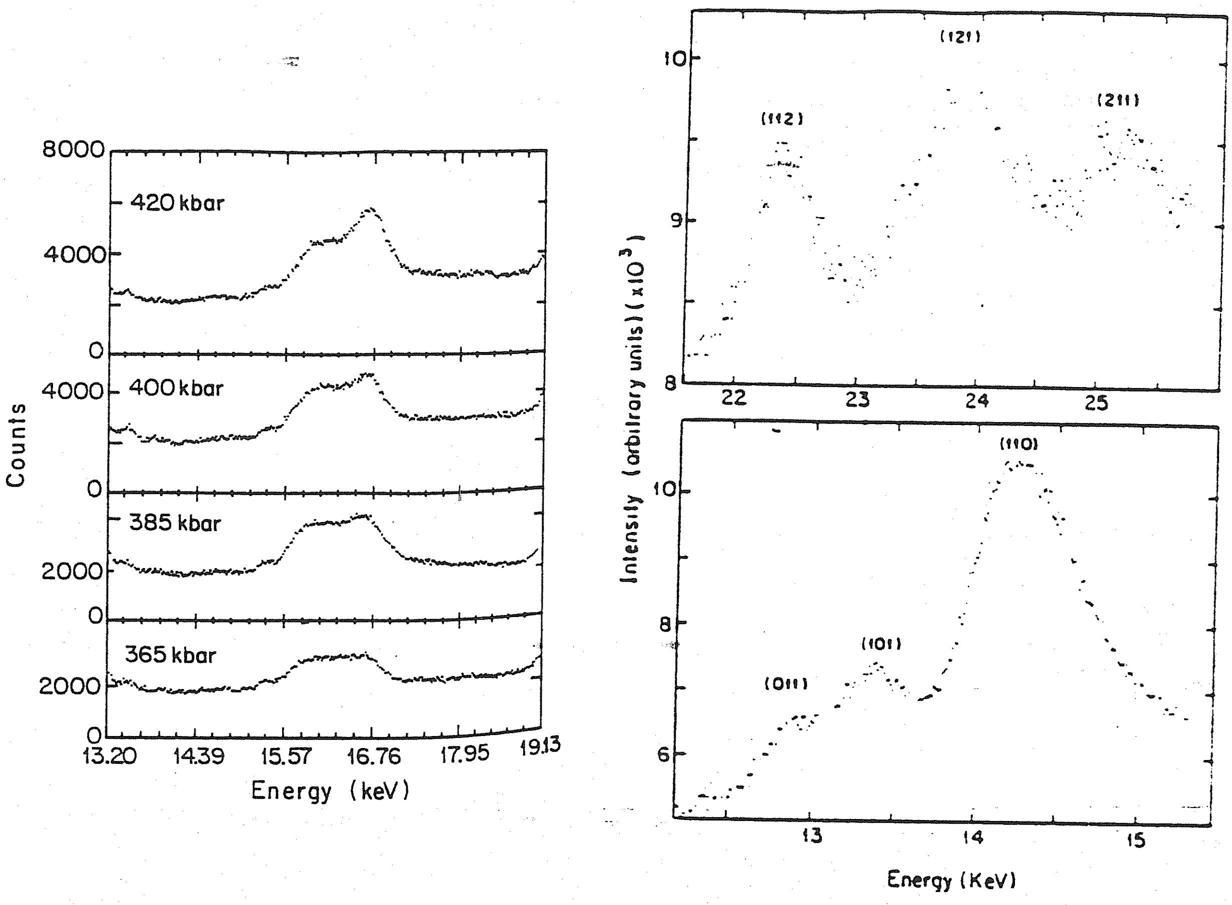
As a general rule, the compressibility of the alkali halides increases with increasing the atomic number of the ions in the crystal. Because of this, the cesium iodide represents the best candidate for studies on high pressure transitions, because it is the most compressible ionic crystal ($B_0 \simeq 111\ Kbar$) with the smallest energy gap ($E_{gap} = 6.3\ eV$).

The optical absorption edge is measured to study the energy gap under pressure. Some difficulties in the interpretation of the results are due to the excitonic absorption. The first experiment [Asaumi, 1981] was affected by serious inhomogeneity in the applied pressure. As a consequence the extrapolated metallization pressure was underestimated. More recently , new experiments [Itie, 1984; Makarenko, 1984] have predicted the gap closure to occur at a pressure of $95 \div 110 GPa$ and a volume ratio $V/V_0 \simeq 0.50$. The metallization volume ratio was correctly predicted theoretically by Linear-Muffin-Tin-Orbitals calculations [Satpathy 1985], but no estimate of the correspondent transition pressure is presented in such work. Good agreement with the experimental results has been previously obtained by Aidun [Aidun, 1983], which calculated a transition pressure of 100 GPa at a volume ratio $V/V_0 \simeq 0.50$. Reflectivity studies [Williams, 1986; Reichlin, 1986] up to 125 GPa have confirmed such experimental and theoretical results.

The arrangement of the atoms in the crystal at high pressure is studied by X-ray diffraction. A structural phase transition from the B2 structure to a tetragonal structure around 40 GPa ($V/V_0 \simeq 0.54$) has been observed in CsI [Knittle and Jeanloz, 1984 and 1985; Huang, 1984]. Little differences among the results of this works can be attributed to non-hydrostatic effects or sudden variations of pressure, which induce dynamical effects. These can affect seriously the transition pressure as it was observed experimentally [Vohra, Weir at al. 1985].

As for the order of the transition, the interpretation of the experiments is not unique. In fact, Huang [Huang, 1984] suggests that the distortion to a tetragonal phase is first order, while Knittle [Knittle and Jeanloz, 1984 and 1985] estimates it is second order. The difficulties to detect experimentally the order of the transition are due to the impossibility to vary smoothly enough the applied pressure. Recent theoretical investigations about the described structural distortion in cesium halides indicate it be first order like and also our new calculation (see below) confirm this interpretation. This transition is apparent isovolumic, within the experimental uncertainties; this has been supported by all the theoretical investigations.

The compression of the tetragonal phase of the cesium iodide has permitted to observe a further distortion [Asaumi, 1984; Vohra, Wier et. al. 1985] occur at $\sim$ 63 GPa. It has been suggested the hypothesis this structure is an orthorombic like structure (see fig.4a), by invoking symmetry arguments too [Vohra, Weir 1985]. Up to now, the nature of this latter structure has not been explained by any theoretical calculation [Vohra, 1985; Baroni, 1987]. Furthermore, we point out that the experiments cannot exclude other possible structures, because they are performed by x-ray diffraction from powders and in particular they display the splitting of a single diffraction peak (see fig.4.a for Csi, fig.4.b for CsBr and CsCl), which becomes double at the B2 $\rightarrow$ tetragonal distortion and splits further into three peaks at the second structural transition. Then they are able to observe only the variations in the length of the cell axes, but no information is extracted about possible tilting of the angles among those axes. Only x-ray diffraction experiments from crystals or theoretical studies can give a conclusive answer to this problem.



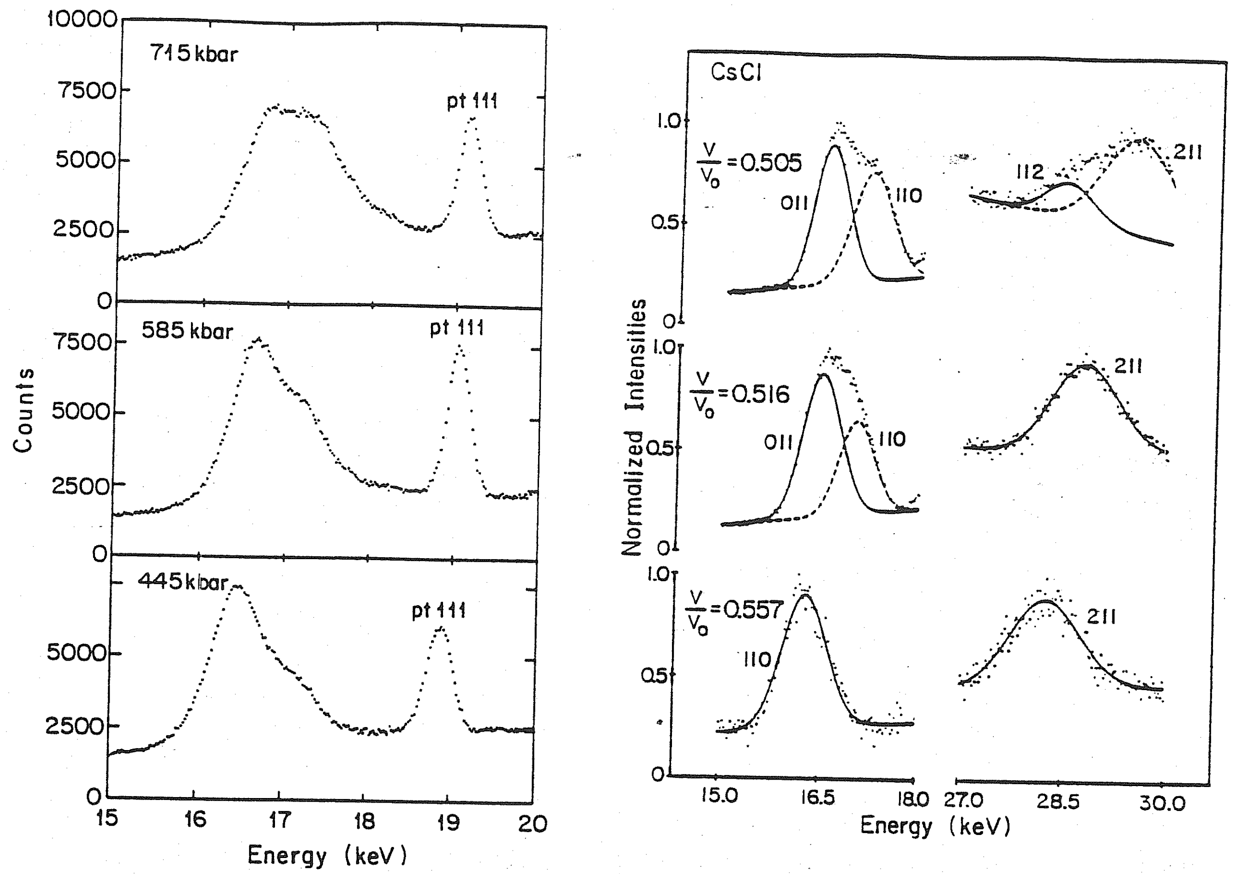
1

2

fig.4a : X-ray diffraction pattern at high pressures for CsI.
(1) cubic to tetragonal distortion; (2) tetragonal to orthorombic distortion.

B.1.2) Cesium Bromide and Cesium Chloride

The transformation of the B2 lattice to a tetragonal structure has been



1 **2**

fig.4b : X-ray diffraction pattern at high pressures for CsBr (1),CsCl (2)

observed experimentally in CsBr [Huang, Brister and Ruoff, 1984; Knittle et. al. 1985] and in CsCl [Brister, 1985] at pressures 53±2 GPa and 65±5 GPa, respectively. Differences in the transition pressures are due to the different stiffness: $B_0^{exp}(CsBr) = 143\ Kbar$, $B_0^{exp}(CsCl) = 167\ Kbar$ consistent with differences in the bulk modulus. The volume ratio at the transition is almost the same for all these compounds ($V/V_0 = 0.53 \pm 0.02$), within the experimental accuracy. These aspects indicate it is a general phenomenon associated to this set of salts.

This high-pressure transformation displays other common features: a) it is isochore type, b) qualitative agreement is shown in the behaviour of the axial ratio (c/a) in the tetragonal phase, where it increases with increasing the pressure up to the highest pressures achieved in these experiments [Knittle and Jeanloz, 1984; Knittle et. al., 1985; Brister, 1985]. About this last aspect, both the experimental measures and our theoretical calculations (see section C in chap.2) indicate that the value of the axial ratio at the transition becomes smaller lowering the compressibility of the material. In, the edge values for cesium halides are: 1.15 for cesium iodide, 1.08 for cesium bromide and 1.05 for cesium chloride.

The further slight distortion of the tetragonal structure observed around 56 GPa in CsI [Asaumi, 1984; Vohra, Weir et. al., 1985], has not be reported for CsCl and CsBr.

CHAPTER 2

Theory of the Lattice Energy, Equilibrium Structure and Pressure Phase Transitions

The structural properties of the alkali halides are from a long time the subject of many theoretical investigations. Several models have been proposed to tackle this problem. Rigid-ion models, such as the semiempirical Born-Mayer model [Tosi (1964)] and the Thomas-Fermi approach of Gordon and Kim [Gordon (1972)], produce only partial successes. Generally, they are not in agreement with experimental quantities at high pressure (transition pressure and volume variation at the structural transitions), while they determine almost quite well the zero pressure features (equilibrium lattice constants and bulk moduli). These deficiencies of the rigid-ion models are largely due to the poor transferability of the employed potential, which is not able to adapt itself to the modifications of the structure. Therefore, first-principle calculations are necessary to describe the behaviour of these compounds on a wide range of the phase diagram. In this chapter, we describe some of the techniques presented in the literature and their capability to predict the experimentally observed structures and the structural phase transitions.

The actual structure of a crystal is determined by the Gibbs free energy,

$$F = U + PV - TS. \tag{2.1}$$

At zero pressure and absolute zero temperature the system crystallizes in that structure showing the lowest internal energy (U). The theoretical prediction of the stable structure is often complicated by the presence of competitive structures which differ very little in energy.

A) Born Model

Historically, the first attempt to describe the structural properties of the ionic crystals was based on semiempirical models. The Born model was largely applied to these compounds [see: Tosi, 1964 and references therein], however this approach is not completely satisfactory. It treats the ions as pointlike charges, whose electrostatic interactions give rise to a net binding (Madelung energy), as each ion is surrounded by ions of opposite charge. To stabilize the system and to avoid its collapse, the attractive forces are balanced by the so-called overlap repulsive forces, which prevent the interpenetration of the ions. Typically, the Born repulsive interactions decrease the binding energy only by about 10% (at zero pressure), since the ions are fairly hard. The explicit form of the repulsive interaction is to a large extent arbitrary: in the literature it is often descibed by a negative power of the interatomic distance, or by an exponential form. Generally, this model shows a poor transferability, which implies a serious difficulty to describe the behaviour of the crystal under pressure or at the phase transitions. In other words, it works well only in that region of the phase diagram where the repulsive potential has been fitted to the experimental parameters. Moreover, the structural stability of the cesium halides is erroneously predicted. In fact, the Born model predicts the rocksalt structure to be the stablest for all the alkali halides (see e.g.: fig.5).

Also the transition pressure for the $B1 \rightarrow B2$ distortion is always largely overestimated [Fumi and Tosi 1962, 1963].

Recently, a version of this model was employed [Vohra, Duclos, 1985] to explain the instability of the B2 structure in the cesium halides at high pressure. In this paper, thermal contribution to the energy and noncentral forces are neglected: the energy is approximated to the static part, as a sum of attractive Madelung energy and a Born-Mayer type repulsive interaction

$$F = -\frac{Z^2\ e^2\ \alpha}{a} + \sum_j \frac{B_r}{r_j^n} \quad . \tag{2.2}$$

Here a is the lattice parameter for the cubic phase, α is the Madelung constant, r_j is the interatomic distance, and summation over index j includes the eight first-nearest neighbours and the six next-nearest neighbours. For the tetragonal

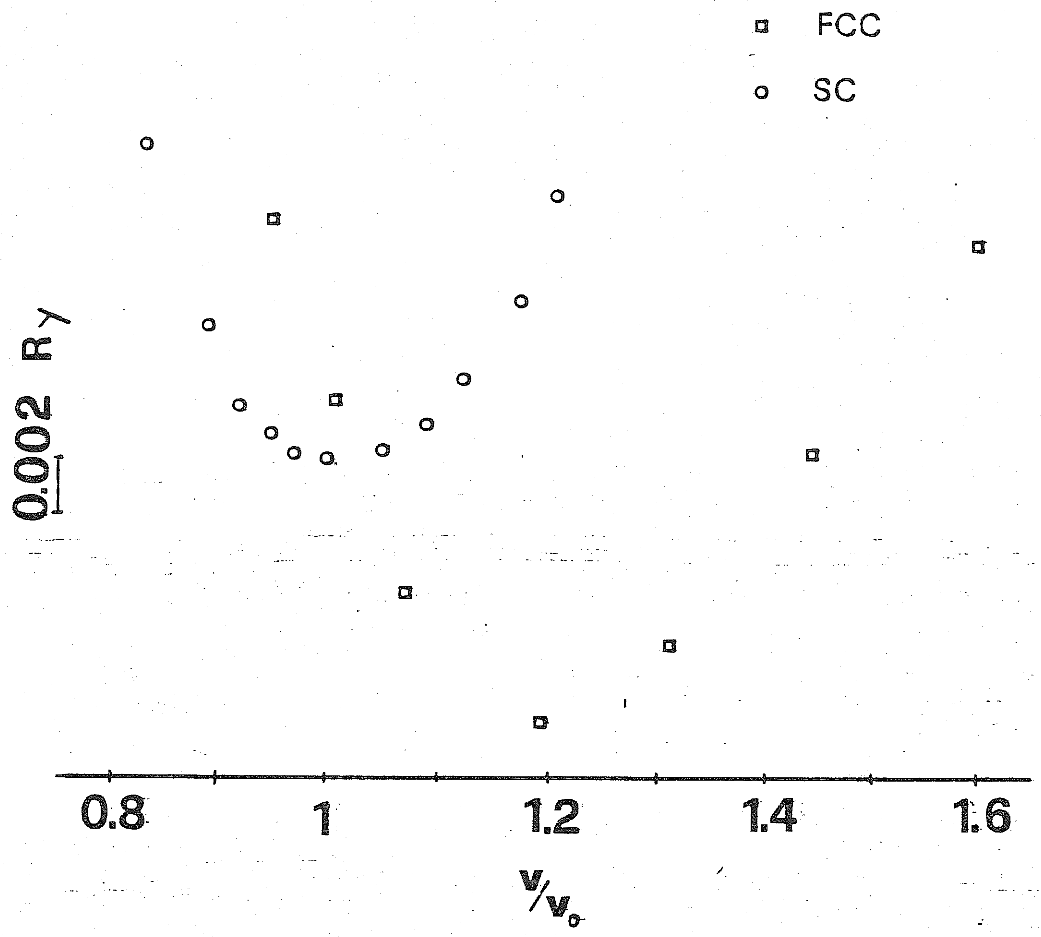


fig.5 : Cesium Iodide. Total lattice energy for the simple cubic phase (circles) and the rocksalt phase (squares) versus volume ratio.

phase these fourteen atoms are taken into account to evaluate the repulsive contribution to the energy, where the six next-nearest neighbours split into four at a distance a and two at a distance c. The parameter B_r is calculated by imposing the equilibrium condition of the energy at the observed lattice constant. This quantity depends only on the exponent n of repulsive potential, which is chosen in such a way to reproduce the bulk modulus. This simple model has been applied explicitly by the authors [Vohra, Duclos, 1985] only to the cesium iodide, however their conclusions can be in principle extended to the whole set of cesium halides displaying the B2-structure at zero pressure (CsCl, CsBr, CsI).

A.1) Application to Cesium Halides

For the case of CsI, the authors [Vohra, Duclos, 1985] have put n=13. This choice does not allow a good description of the crystal properties at atmospheric pressure, as it introduces an error greater than 25% on the evaluation of the Bulk modulus for cesium iodide and even greater for cesium bromide and cesium chloride. In the case of cesium iodide the value n=11 would give a more realistic prediction of the Bulk modulus. However, with this choice of n is possible to describe only partially the behaviour of the system at the structural transition. In fact, the theoretical value of $V/V_0 = 0.515$ (with n=13) at the phase transition is in agreement with the experimental value of 0.53 ± 0.02 for cesium halides. Also the qualitative trend for growth of the axial ratio c/a with the pressure is correctly predicted, though overestimated.

In the Vohra's paper, it is reported that the authors have attempted to describe the structural instability in the cesium halides by the Huggins-Mayer potential with Pauling coefficients. However they note that this approach gives a transition volume which is too low (less than 0.3); for this reason they indicate their model as the practicable way to describe the phenomenon. We observe that the comparison is inconsistent, because the cited parameters and the coefficients are adequate only for salts stable in the rocksalt structure [Tosi, 1964], then their use is not justified in the present case.

To verify the goodness of this model we have attempted to extend its application to the other two cesium halides (CsBr, CsCl) and to rubidium bromide, but the conclusions are not satisfactory. The first important deficiency regards the prediction of the stable structure at zero pressure. As any other Born-Mayer model [Tosi, 1964] it predicts the rocksalt structure to be the stable for cesium halides at zero pressure (see fig.5 for the case of cesium iodide).

The authors have also investigated the possibility of further distortion of the tetragonal lattice into an orthorombic lattice, but they found the minimum in the lattice energy occurring at $b/a = 1$, for every value of the pressure. We have extended this research to include also a possibly stronger distortion, taking into account a modification of the angles in the cell (monoclinic lattice). Because the concept of shell of neighbourhoods misses its meaning by lowering the symmetry of the lattice, in order to take into account all the important contributions to the repulsive energy we have included in the summation a larger number of ions, choosing all those that are found inside a sphere centered on the atom in the origin, with a radius 2.5 times the zero-pressure lattice constant. The lattice parameters have been varied in the range of the experimental values [Vohra,Weir, 1985; Asaumi, 1984], but no new stable minimum has been found. As an example, we report in fig.6 the energy surface at fixed $V/V_0 = 0.49$ and $c/a = 1.25$ as a function of the axial ratio b/a and the angle α between the axes a and b of the cell. The failure of this model to describe the distortion of the tetragonal lattice is not surprising, because as it is reported above its range of applicability is never so wide to predict well the full phase diagram of a compound.

According to the experiments [Brister,1985; Knittle and Jeanloz, 1984; Knittle et. al., 1985] the edge value of the axial ratio c/a at the transition is 1.08 and 1.05 for CsBr and CsCl, respectively. Applying the Vohra's model to the cases of CsBr and CsCl, we have found a more and more poor agreement of the theoretical predictions with the experimental observations. Infact, the model predicts a value greater than 1.20 for both them, and also the estimation of the Bulk moduli suffers of a serious error: about 27% for both CsBr and CsCl.

We have tried also to introduce a trivial modification of the model parameters, without founding any increase in the quality of the description of all the cesium halides. On the contrary, if the exponent n assumes a value lower than 13, then the volume ratio V/V_0 at the transition to the tetragonal structure is largely understimated. In conclusion, we may say this way to describe the instability of the CsCl structure in ionic solids at high pressure is largely unsatisfactory, because its poor range of applicability and incorrect predictions.

The value of the model is that, though it suffers of the above drewbacks, it correctly displays the mechanism of the transition, which is due to the balance between the repulsive and attractive contributions to the energy. The Madelung

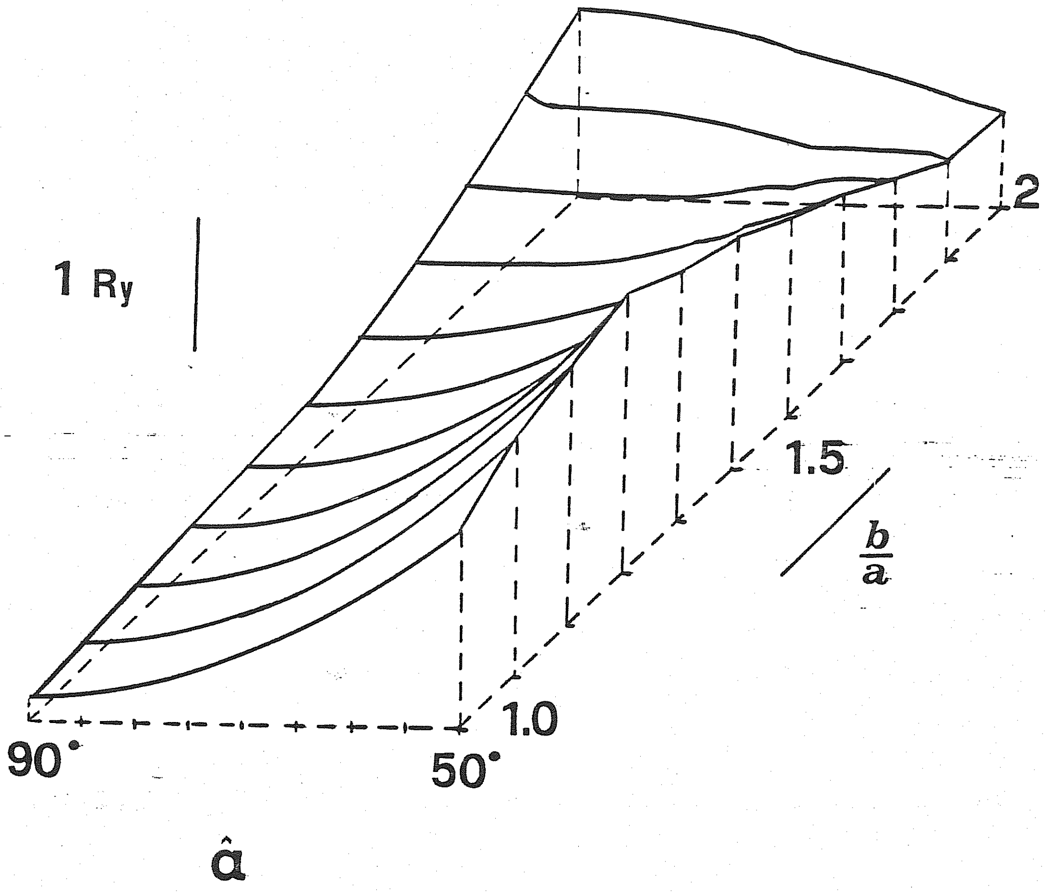


fig.6 : Cesium iodide. Lattice total energy surface as a function of the axial ratio $\frac{b}{a}$ and α

energy increases with increasing c/a and opposes the distortion. The distortion is favored by the resulting sharper decrease in the repulsive energy due to the first-nearest neighbours. Note, however, that it is the increase in the repulsive energy of the second-nearest neighbors which produce a minimum in the total

	CsCl	CsBr	CsI
B_o^{ex}	167	143	111
B_o^{th}	212	182	140

(Kbar)

tab.1 : Theoretical and experimental bulk moduli for cesium halides.

energy curve at c/a greater than 1 for volume ratios smaller than $V/V_0 = 0.515$.

Further, we have applied this simple model to the description of the Rubidium Bromide, but we have found only partially agreement with experimental results. For this salt the exponent $n = 9$ has been chosen in order to fit the lattice constant and the bulk modulus measured experimentally at zero pressure and room temperature. As expected, the structure stability is correctly predicted (see fig.7). However, the model is not able to predict accurately the transition pressure from the B1 to the B2 structure. The predicted transition pressure is almost four times larger than the experimental value ($P_T \simeq 5\ Kbar$) [Cohen and Gordon, 1975].

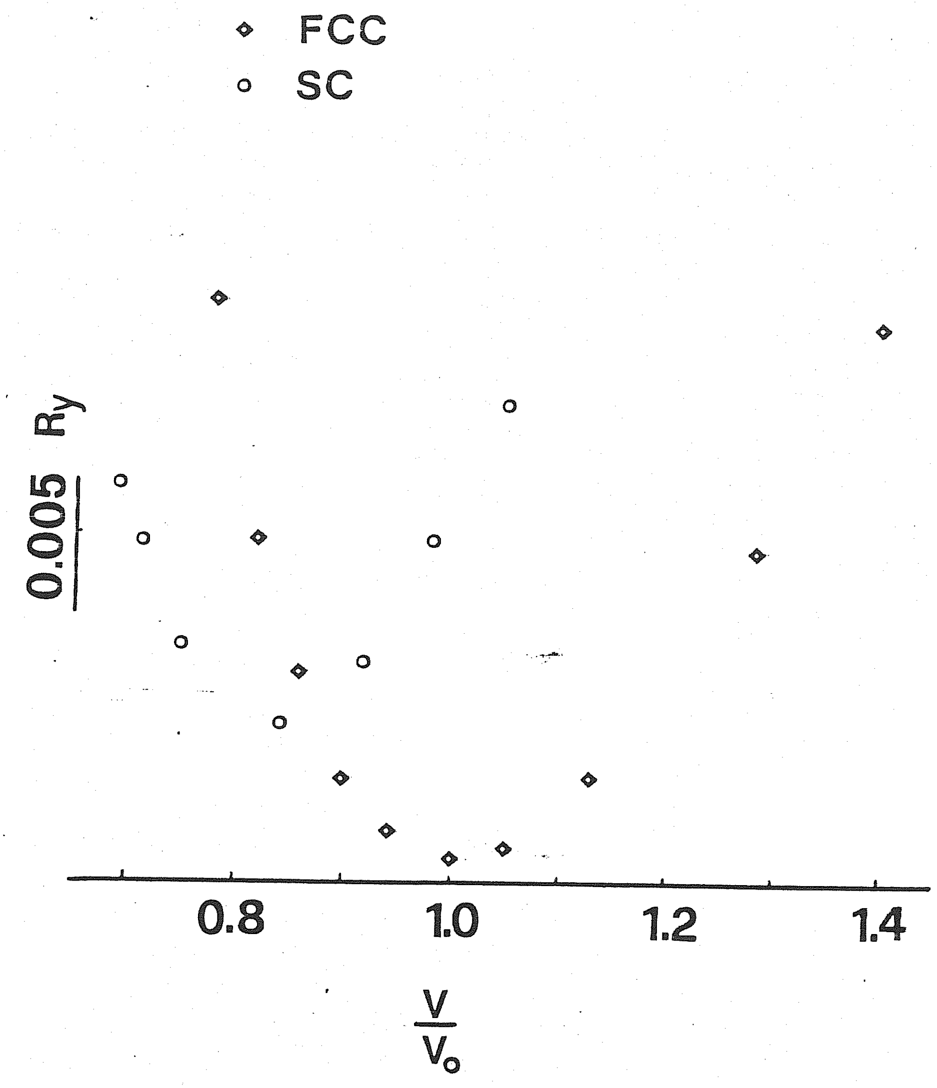


fig.7 : Rubidium Bromide. Lattice energy for the simple cubic phase (circles) and the rocksalt phase (squares) versus volume ratio

B) A Brief Review of Structural Calculations on Alkali Halides

In this paragraph, we report a brief review of some models and *ab − initio* methods which have been used to treat the structural features of the alkali halides. The paragraph is divided in two section: the first is devoted to the rigid-ion models and the second to the LDF formalism and the LMTO method.

B.1) Other Rigid-Ion Models

Apart from the semiempirical Born-Mayer model, the rigid ion approximation has been adopted in some others models, which describe the structural properties of the matter. For example, we may quote the Thomas-Fermi local-density model proposed by Gordon and Kim [Gordon, 1972]. It describes the electron density of the system as a sum of the two separate charge densities for the two chemical species, and the non-Coulomb part of the interaction potential is calculated using the electron-gas energy expression for the density. For the evaluation of the kinetic-energy, a Thomas-Fermi like definition is adopted. Further assumptions introduced in the model are: a) the system is made of free ions; b) the interactions of the ions is the sum of all pairs interactions; c) the short-range interactions are restricted to the nearest-neighbour pairs only. The application of this approach to the alkali halides [Kim, 1974; Cohen and Gordon, 1975] is only partially satisfactory. In fact it predicts well the cohesive energies and the nearest-neighbour distance in all the alkali halides which exhibit the rocksalt structure. Also the structural stability of these salts is correctly predicted [Cohen and Gordon, 1975]. However, the agreement of the the estimated transition pressures for the $B1 \rightarrow B2$ transformation with the experiments is generally poor, though it is better than within the Born-Mayer model (see tab.2). For the softer salts (rubidium halides) the transition pressure is overestimated by a factor $2 \div 3$, while for the sodium salts it is underestimated. Only for the potassium halides we find a fair agreement with the experiments. To the best of my knowledge, this model has not been applied to cesium halides.

B.2) *Ab – Initio* Calculations

As described above, up to a decade ago many of the theoretical approaches to the study of the structural properties of the alkali halides were based on model calculations. The solid is modeled by point ions attracting each other

	G.-K.	BORN	Experimental values^{b}					
			I	II	III	IV	V	VI
LiF	550	310	$>100^{c}$					
LiCl	160	110	>100					
LiBr	110	105	>100					
NaF	142	200	>100		>200			16.8^{d}
NaCl	49	74	20		>250	29	>50	18^{e}
NaBr	35	53	>100					
KF	51	88	>100	20				
KCl	21	36	20	19.7	20	20	20	
KBr	17.0	29	19	18.1		18.5		
RbF	30	68	>100	11.8				
RbCl	14.0	31	5.5	4.9				5.4^{f}
RbBr	12.4	25	5.0	4.5				

G. K. : Gordon R.G., Kim Y.S. : P.R. 9, 3548 (1974)

tab.2 Theoretical and experimental values for transition pressure

electrostatically and held apart by some short range potential. The parameters in the model are either fitted to experimental measures [Tosi, 1964; Vohra and Duclos, 1985] or calculated from ionic charge densities [Gordon, 1972]. These models have successfully described the basic properties of bonding. The first *ab-initio* attempt in this direction was the Hartree-Fock calculation by Löwdin [Löwdin, 1956]. At present both Hartree-Fock theory and density functional methods are employed.

As for the Local Density Formalism, we can mention some studies of the equilibrium properties of NaCl and KCl [Andreoni, 1982; Froyen, 1984 and 1986], and of the structural instability under pressure in CsI [Baroni, 1987] performed by *ab-initio* pseudopotentials technique, and the study of the same structural transformation in CsI by the LMTO method [Christensen, 1985].

LDF formalism

For a system of N interacting electrons in the presence of an external potential v(r), the non-relativistic Schrödinger equation is

$$[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|}]\ \Psi(\{\mathbf{r}_i\}) \;=\; E\Psi(\{\mathbf{r}_i\}). \qquad (2.3)$$

The density-functional theory [Hohenberg 1964] permits in principle to determine the ground state properties of the system using the particle density, n(**r**), as the free variable. Further, it's possible to reduce the many-body equation (2.3) to a single particle equation [Kohn 1965]. The basis of this theory is given by the Hohenberg-Kohn theorem [Hohenberg 1964]

" Let $n(\mathbf{r})$ be a density distribution, associated with a ground state in the external potential $v(\mathbf{r})$, and let $n'(\mathbf{r})$ be similarly with $v'(\mathbf{r})$. Then, if $n'(\mathbf{r}) = n(\mathbf{r})$, $v'(\mathbf{r}) = v(\mathbf{r}) + const$ ".

This theorem establishes that the particle density determines the external potential a part from a trivial additive constant. In conclusion, v(**r**) is a functional of n(**r**), then also the Hamiltonian is fully determined by n(**r**).

Assuming a nondegenerate ground state (the discussion can be extended to the degenerate case too), is easy to understand that also the wavefunction is a functional of n(**r**). Finally, we may conclude that all the properties of our system can be determined starting from the knowledge of n(**r**). In particular, the energy of the system is defined as a functional of n(**r**):

$$E_v[n(\mathbf{r})] \;=\; T_s[n(\mathbf{r})] + \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + \int n(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + E_{xc}[n(\mathbf{r})], \qquad (2.4)$$

where T_s is defined as the kinetic energy of a non-interacting electrons system with the same density n, the second term defines the electrostatic (classical) energy, the third is the interaction with the external potential, and the fourth is the so-called exchange-correlation energy. The minimization of this expression respect to the particle density allows to determine the ground state energy.

Starting from the stationarity of $E_v[n(\mathbf{r})]$, single particle self-consistent equations have been deduced [Kohn, Sham 1965]:

$$[-\nabla^2 + v_{eff}(r)]\psi_i(r) = \epsilon_i\psi_i(r), \tag{2.5}$$

where

$$v_{eff} = v(\mathbf{r}) + 2\int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc}(r) \tag{2.6}$$

and

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \tag{2.7a}$$

$$n(\mathbf{r}) = \sum_i |\psi_i(r)|^2 \tag{2.7b}$$

(the summation in eq.(2.7b) is restricted to the lower N occupied states).

The practical solution of the Kohn-Sham equations requests the knowledge of the exchange-correlation term in eq.(2.6). In order to reach such scope, we need to introduce some approximations. For a system whose density n($\mathbf{r}$) is a slowly varying function of r the following, so-called local density approximation is applicable:

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}(n(\mathbf{r}))\cdot n(\mathbf{r})\; dr,$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy, per particle of a uniform electron gas of density n [Ceperley 1980].

This approximation would, *a priori*, appear very questionable when applied to atoms, molecules and solids, since the necessary condition of "slow" variation of n($\mathbf{r}$) seem not to be fulfilled. Experience has shown, however, that it gives surprisingly good results.

As for the cesium halides behaviour under high pressures, very interesting results have been obtained by the application of the Linear-Muffin-Tin-Orbital (LMTO) method. For the first time, the structural transformation observed in CsI has been described by $ab-initio$ calculations within the Local-Density Approximation (LDA) [Christensen, 1985]. Then the total energy functional is given by eq.(2.4), that we may rewrite as:

$$E = T_S + U_c + U_{xc}, \tag{2.8}$$

In the Muffin-Tin model the coulombic (U_c) and the exchange-correlation (U_{xc}) terms take the following forms:

$$U_c = \int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\ d\mathbf{r}$$

$$U_{xc} = N \sum_i \int_{\Omega_i} \epsilon_{xc}[\rho_i(\mathbf{r})]\ \rho_i(\mathbf{r}) d\mathbf{r}\ +\ \int_{\Omega'} \rho_0 \epsilon_{xc}[\rho_0]\ d\mathbf{r}$$

.

The system is formed by N cells, each of them contains n atoms, labelled by the index i. Then the space is divided into nonoverlapping Muffin-Tin spheres (Ω_i), centered on the lattice sites and an interstitial region (Ω'). Then the total charge density in the coulombic term is:

$$\rho(r) = \sum_{\mathbf{R},i} \{[\rho_i(|\mathbf{r}-\mathbf{R}-\mathbf{h_i}|) - \rho_0]\Theta_i - Z_i\delta(\mathbf{r}-\mathbf{R}-\mathbf{h_i})\} + \rho_0.$$

The two contributions in brackets are due to the electrons in the MT sphere and to the nuclear charge. The vectors $\mathbf{h_i}$ determine the atomic positions inside the cell.

In the Atomic Sphere Approximation (ASA), the Muffin-Tin spheres are replaced by overlapping atomic spheres and ρ_0 is written as the average of the electron densities on the atomic-sphere surfaces. However, the simple ASA is not able to describe the structural transition, in fact it indicates the cubic structure as the only stable lattice for the crystal. The correct description of the transformation has been obtained by including non muffin-tin corrections in the electrostatic interaction energy. This term is strongly volume dependent and, for a volume ratio smaller than 0.53, drives the system into a tetragonal phase, characterized by an increasing value of the ratio c/a with increasing the pressure. Also the transition-pressure predicted theoretically is in good agreement with the experimental value. The total-energy curves show a structural bistability (two different minima for two different structures) around the transition, which disappears at a volume ratio $V/V_0 = 0.48$.

The same self-consistent technique has been employed in the study of the metallization of CsI under pressure [Satpathy (1985)] and to calculate the electron energy bands for all cesium halides [Satpathy (1986)]. The former study gives also some indications that a distortion of the tetragonal structure to the orthorombic one favours the gap-closure and then the metallization transformation. This observation would be in agreement with experimental studies on CsI, which report a further structural transition to a probable orthorombic lattice. However, these calculations hve not been able to show that the orthorombic structure is stabler than the tetragonal one.

The band structure calculation performed by the LMTO method shows a substantial agreement with the experiments. The calculated lattice constants down the series from CsCl to CsI increases in magnitude consistently with experiments. The cohesive energy shows the correct physical trend:

$$\mathbf{E}^{\mathbf{cohes}}(\mathbf{CsCl}) > \mathbf{E}^{\mathbf{cohes}}(\mathbf{CsBr}) > \mathbf{E}^{\mathbf{cohes}}(\mathbf{CsI}) \ .$$

However, the quantitative comparison is not quite satisfactory. This study confirms of the strict similarity among these compounds. About the zero pressure predictions, the technique does not give a good estimate of the bulk modulus for CsBr and CsCl; a discrepancy of the same order can be found in our $ab-initio$ pseudopotential study for CsBr (see below).

C) *Ab − initio* Pseudopotential Technique

The self-consistent *ab − initio* pseudopotential technique within the Local Density Functional formalism [Hohenberg,(1964);Kohn,(1965)] has been largely applied to study electronic and structural properties of semiconductors [McMahan, 1981]. It has allowed to predict structural stability and pressure induced phase transitions for several compounds and elementary crystals [Yin,(1982)].

As we have explained in the previous paragraphs, its application to ionic crystals is very recent and only few compounds have been analyzed [Andreoni, 1982; Froyen, 1984 and 1986; Baroni 1987].

C.1) THEORY

The first step in the resolution of the Kohn-Sham equations is the determination of the external potential $v(r)$ (see eq.(2.6)). In the case of a solid system, the potential is that due to the nuclei placed on the lattice sites. Since the effect of the core electrons on the chemical and structural properties is negligible, we fix our attention only on the valence electrons. This approach is the so-called pseudopotential method and allows to reduce considerably the computational effort. In this way we are able to introduce an effective pseudopotential, which takes into account the interaction of the valence electrons with both nuclei and core-electrons.

The *ab − initio* nonlocal norm-conserving pseudopotentials, commonly applied in such a type of calculations, are produced under the condition that they accurately simulate valence-electrons core interaction in the atom. This means that the pseudopotential atomic results (e.g., excitation atomic energies and atomic energy levels) are approximately the same as the correspondent all-electron results. It has been shown [Yin,Cohen (1982)] that if such a condition is satisfied in the single atoms of the compounds, then it will be satisfied in the crystalline system too. However, it does not exist only one way to generate *ab − initio* pseudopotentials. A method to generate the pseudopotentials was proposed by Kerker [Kerker (1981)]. It starts from self-consistent atomic calculations and modifies the wavefunctions in such a way to satisfy an assigned set of conditions for the pseudowavefunctions. In this scheme, the actual shape of the atomic valence wavefunction inside the core region is replaced by a convenient analytical form

$$F(r) = r \cdot R(r) = r^{l+1} \cdot f(r) \quad ,$$

where $R(r)$ is the radial part of the pseudo-wavefunction and l denotes the angular momentum quantum number. The function $f(r)$ is chosen to give a smooth non-singular potential. The conditions to satisfy are the following: 1) The real and "pseudo" atoms have the same valence eigenvalues for some chosen electronic configuration. 2) The pseudo-wavefunction R(r) is nodeless and is identical to the real valence wavefunction at and beyond a chosen core radius r_c. 3) Both the first and the second derivatives of the wavefunction F are matched to the real values at r_c. 4) The pseudo-charge contained in the sphere with the radius r_c is identical to the real charge in that sphere (norm-conserving).

To calculate the ionic pseudopotential one follows this way: starting from the pseudowavefunctions $F(r)$, one calculates the atomic pseudopotential, V_{ps}^{at}, by inverting the Schrödinger equation for the atom, and at the same time computes the charge density due to the valence electrons (pseudo charge density $\rho_{ps}(r)$). The knowledge of $\rho_{ps}(r)$ allows to calculate the Hartree and the exchange-correlation contributions to the atomic potential. Finally, the ionic pseudopotential is given by subtracting these two quantities to the atomic pseudopotential

$$V_{ps}^{ion} = V_{ps}^{at} - V_H - V_{xc} \quad .$$

The norm-conserving property is important in total energy calculations, because it ensures the transferability of the pseudopotential from the atom to complex systems.

In this case a plane-wave basis set is introduced to represent the valence pseudowavefunctions. There are several important reasons to prefer this choice of the basis set: 1) the contributions to the total energy (see eq.(2.4)) can be calculated explicitly; 2) the degree of accurancy in the description of the charge density is almost independent from the crystal structure, then it permits to compare total energies calculated for different structures and to study eventual structural phase transitions.

We write the total energy for a solid in this way:

$$E_{tot} = E_{kin} + E_{ec} + E_H + E_{xc} + E_{cc} \quad . \tag{2.9}$$

The contributions in the r.h.s. of eq. (2.9) have the following meaning, in the order: the electronic kinetic energy, the electron-core interaction energy, the Coulombic electron-electron interaction energy (Hartree term), the electronic exchange and correlation energy, and the Coulombic core-core interaction energy (Ewald term). Where the energy terms E_{ec} , E_{cc} and E_H don't contain the infinite contributions due to the long-range Coulomb interaction, because the global charge neutrality of the full crystal produces their mutual cancellation [Ihm (1979)]. Finally, the exchange-correlation energy is a functional of the pseudo-charge density $\rho(r)$: $E_{xc} = E_{xc}[\rho(r)]$, and within the local density approximation,

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\epsilon_{xc}[\rho(\mathbf{r})] \; d\mathbf{r}, \tag{2.10}$$

where ϵ_{xc} is a function of $\rho(r)$.

The explicite expressions of the terms in eq. (2.9), referred to the unitary crystalline cell, are given by

$$E_{kin} = \frac{1}{N}\sum_{i,\mathbf{G}} n_i \frac{\hbar^2|\mathbf{k}_i + \mathbf{G}|^2}{2m} |\psi_i(\mathbf{k}_i + \mathbf{G})|^2, \tag{2.11}$$

$$E_{ec} = \frac{1}{N} \sum_{i,\mathbf{G},\mathbf{G}'} n_i\psi_i^*(\mathbf{k}_i + \mathbf{G})\psi_i(\mathbf{k}_i + \mathbf{G}')\{V_{ps}(\mathbf{k}_i + \mathbf{G}, \mathbf{k}_i + \mathbf{G}) +$$

$$\delta_{\mathbf{G},\mathbf{G}'} \frac{1}{\Omega_c} \int \frac{ze^2}{r} \; d\mathbf{r}\}, \tag{2.12}$$

$$E_{xc} = \frac{\Omega_c}{2} \sum_{G} \rho^*(\mathbf{G})\epsilon_{xc}(\mathbf{G}), \tag{2.13}$$

$$E_H = \frac{\Omega_c}{2} \sum_{\mathbf{G}\neq 0} \frac{4\pi e^2}{|\mathbf{G}|^2} |\rho(\mathbf{G})|^2, \tag{2.14}$$

$$E_{cc} = \frac{1}{2} \sum_{S,S'} Z_S Z_{S'} e^2 \{ \frac{4\pi}{\Omega_c} \sum_{\mathbf{G}\neq 0} [\frac{1}{|\mathbf{G}|^2} cos(\mathbf{G} \cdot (\tau_S - \tau_S)) exp[\frac{|\mathbf{G}|^2}{4\eta^2}]] -$$

$$\frac{\pi}{\eta^2 \Omega_c} + \sum_l [\frac{erfc(\eta x)}{x}]_{x=|l+\tau_s-\tau_s|} - \frac{2\eta}{\sqrt{\pi}} \}. \tag{2.15}$$

Where n_i and ψ_i are the occupation number and the pseudowavefunction of the i-th state, respectively. N and Ω_c are, respectively, the number of cells in the crystal and the cell-volume. The direct and reciprocal-lattice vectors are indicated by l and G, respectively, and the atomic positions inside the cell by τ_s. The parameter η controls the convergency of the Ewald summations, for the alkali halides it's generally chosen equal to one.

C.2) PREVIOUS CALCULATIONS

The first *ab-initio* calculation applied to alkali halides has regarded the sodium chloride [Andreoni (1982)] and particularly the cohesion at zero pressure. The estimates of the lattice constant and bulk modulus are in good agreement with the experimental results. The main goal of this study is the correct description of the chemical bonding (previous empirical pseudopotential approaches have erroneously indicated a non-negligible covalent contribution to the chemical bond in alkali halides [Nagel (1976)]) and the demonstration of the isotropic deformation of the electronic charge distribution either when the ions are brought together to form a crystal or when the crystal is subject to a homogeneous deformation (e.g., due to hydrostatic pressure), which directly affects the total energy terms as a function of the lattice constants.

More recent studies on NaCl and KCl, performed by Froyen and Cohen [Froyen (1984) and (1986)], have confirmed the principal results described above [Andreoni (1982)] and furthermore they predict some dynamical features and solid-solid structural transitions. Also the correct lattice structure at zero pressure is correctly predicted by comparing the total energy curves, as function of the lattice constant, for different structures: the rocksalt phase is predicted to be stable at equilibrium (see fig.8)

A brief comment has to be devoted to the prediction of the transition-pressure for the pressure-induced transformation from rocksalt (B1) structure to cesium-chloride (B2) structure. In the case of the sodium-chloride the agreement with the experimental results [Basset (1968), Piermarini (1975), Sato-Sorensen (1983), Heinz (1984)] is good. On the contrary, for KCl we observe a general disagreement and particularly the transition-pressure is largely underestimated (the error is of the order of 50 per cent). In principal the absolute error introduced in the calculations for both compounds is the same, and it is due to intrinsic limit of the method, however its effect becomes more important for KCl because its higher compressibility and lower transition-pressure.

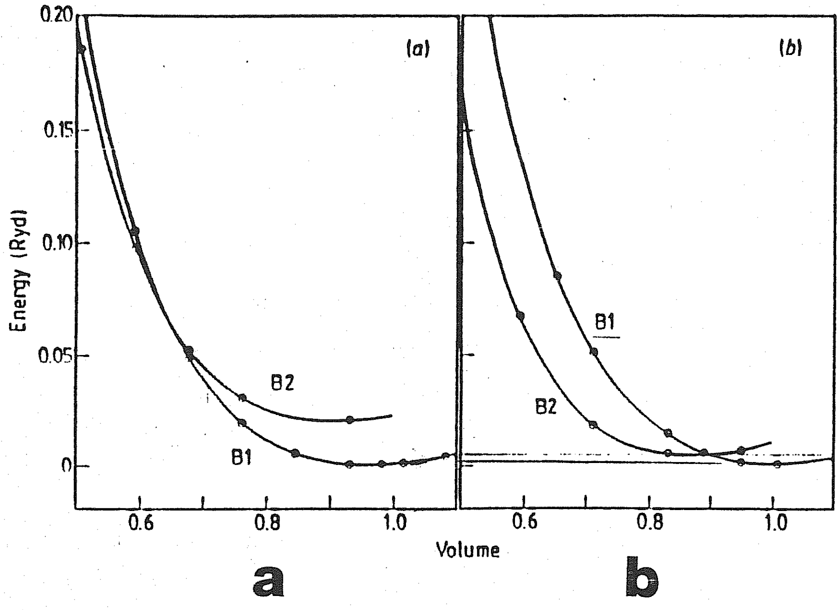


fig.8 : The calculated total energy per molecule as a function of volume for NaCl (a) and KCl (b) in the rocksalt (B1) and CsCl (B2) structures

C.3) NUMERICAL RESULTS and DISCUSSION

C.3.1) CESIUM IODIDE

Here we report few calculations about the zero- and high-pressure behaviour of cesium iodide. Respect to previous analogous calculations [Baroni, 1987], here we adopt an higher energy cutoff (E_{pw}), which allows to obtain a better numerical convergence. Also in the present case, Kerker's pseudopotantials are used. For the cesium atom, it is generated with the inclusion of 5s and 5p states inthe valence shell. This choice is fundamental in order to obtain a stable configuration with decreasing the volume of the unitary-cell in the crystal.

The agreement of the present results with both experimental and theoretical [Baroni, 1987] results is quite good. In particular, no differences are observable in the estimates of the lattice constant and the transition volume ratio ($V/V_0 = 0.54$).

The only important difference between the predictions at the two energy cutoffs (21 Ry and 25 Ry) concerns the observed bistability. In both previous pseudopotential [Baroni (1987)] and LMTO [Christensen (1985)] calculations, the total energy curves versus the ratio c/a at the transition volume ratio and for smaller volumes always show two different minima. One corresponds to the cubic configuration and the second, which is the absolute one, to the tetragonal structure. This shape of the curve indicates the existence of a possible metastable cubic phase. The relative minimum disappears increasing the applied pressure. Increasing the energy cutoff at 25 *Ry*, this shape of the curve is still observable, but less pronounced. In fact, the secondary minimum (metastable cubic phase) disappears more rapidly, see figs.9: already at a volume ratio of 0.52, only the tetragonal phase exists (see fig.9b).

C.3.2) CESIUM BROMIDE

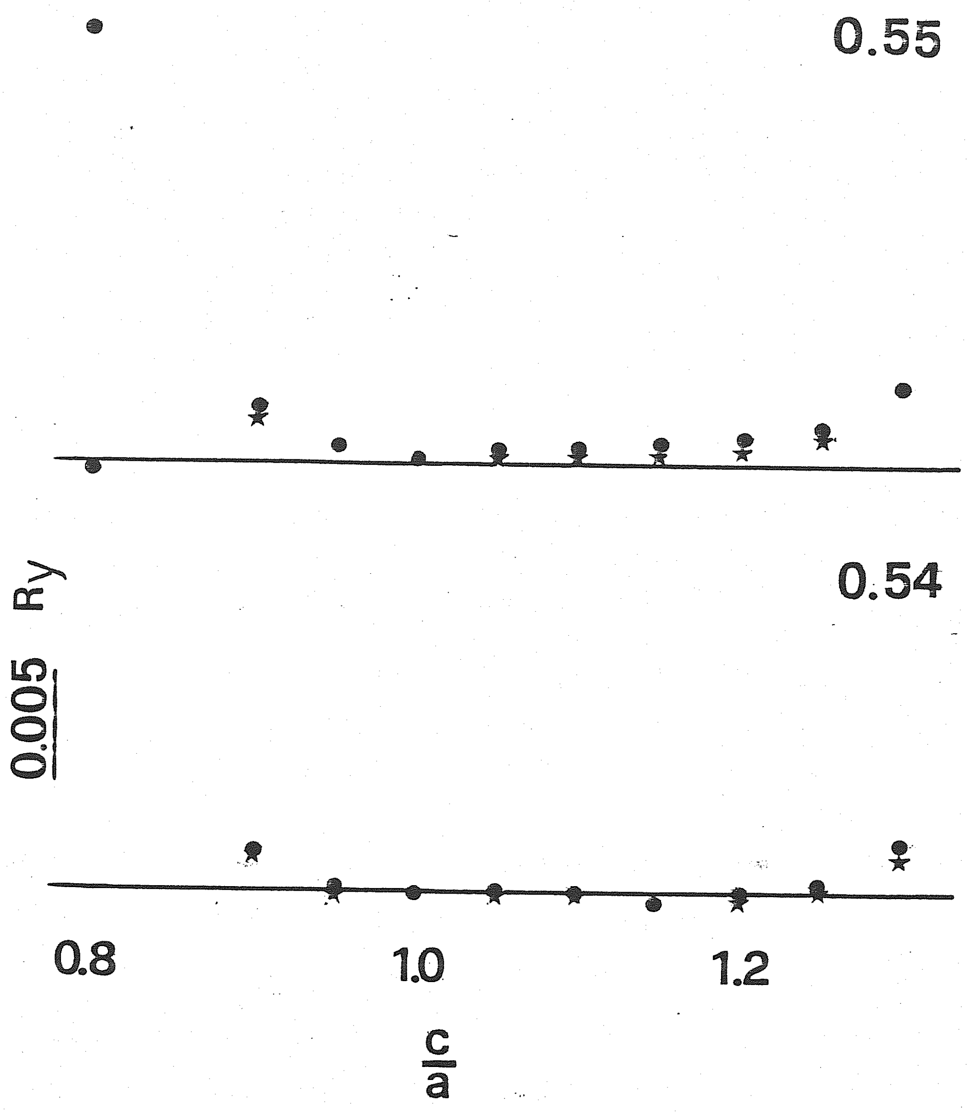


fig.9.a CsI : Total energy curves as a function c/a
[data at 21 Ry (dots);data at 25 Ry (stars)]

As described above, the behaviour of the cesium bromide under high pressures presents several analogies with that of the cesium iodide. With respect to the latter, cesium bromide shows a lower compressibility ($B_0 = 146\ Kbar$). As consequence of this aspect, an higher transition-pressure for the cubic-to tetragonal distortion has been measured experimentally ($P_t = 630\ Kbar$), and also the degree of distortion is less pronounced.

These two aspects are crucial in the study of its pressure induced structural

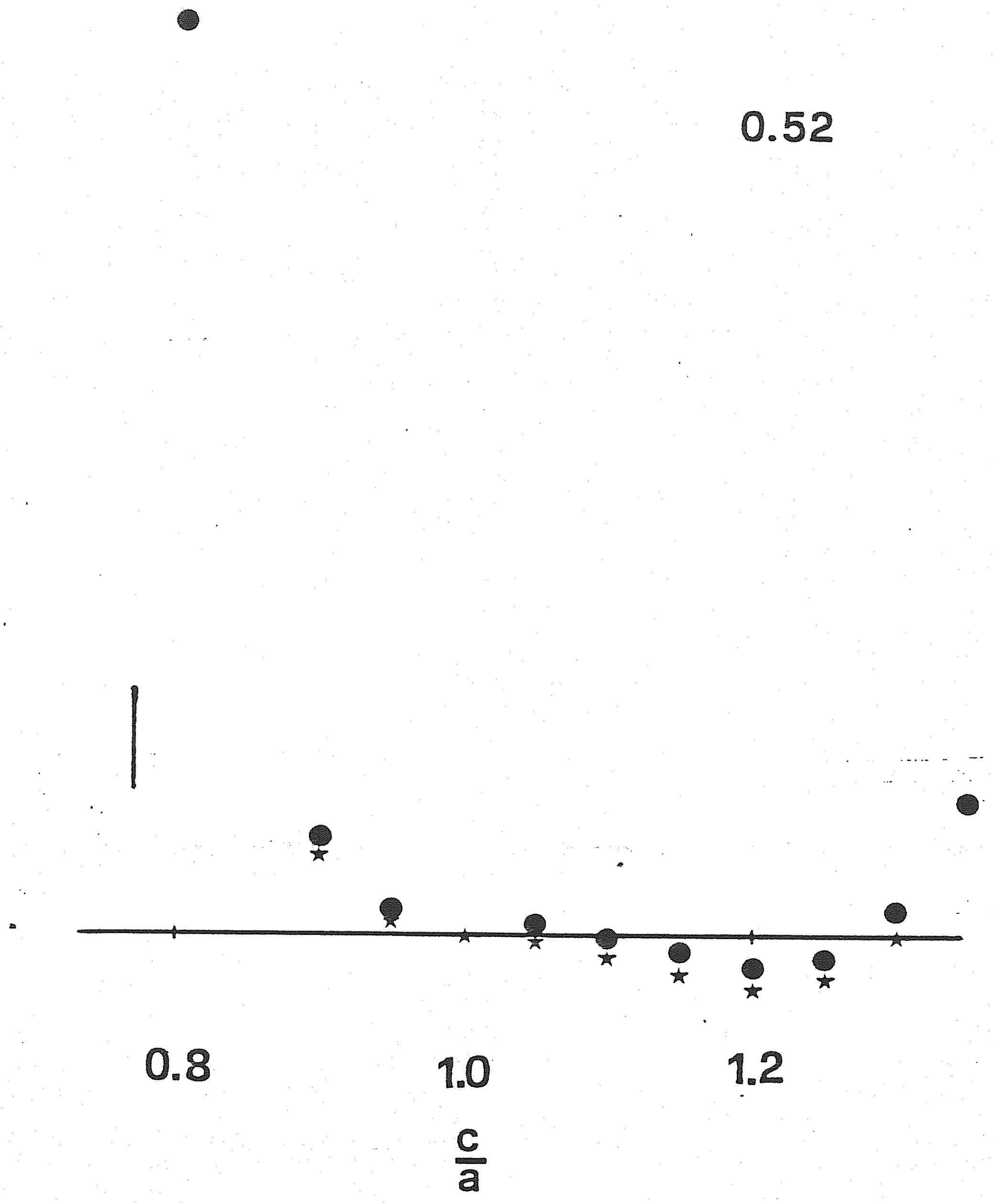


fig.9.b CsI : Total energy curves as a function c/a
[data at 21 Ry (dots);data at 25 Ry (stars)]

instability, because the little deformation of the lattice implies the necessity to discriminate among configurations which differ not only very little in energy, but also are very close in the configuration space.

Zero-Pressure Data

In fig.10 are reported the energy versus volume curves for cesium bromide calculated assuming a cesium chloride structure (circles) and a rocksalt crystal structure (squares). The energy cutoff is fixed at 25 rydberg, which is essential to study the structural distortion at high pressure. The number of special K-points in the irreducible wedge of the Brillouin zone for the cubic phase is 10, while it raises to 18 in the case of the tetragonal phase.

Total energies for different values of the unit-cell volume have been fitted to the first-order Murnaghan equation of state [Murnaghan (1944)],

$$E(V) = \frac{B_0\ V}{B_0'\ (B_0\ -\ 1)} \cdot \{B_0'[1 - \frac{V}{V_0}] - 1 + [\frac{V_0}{V}]^{B_0'}\} + E(V_0)$$

where V_0 is the equilibrium volume, B_0 the bulk modulus and $B_0\prime$ the first derivative of B_0 respect to pressure at $V = V_0$.

In tab.3 are reported the estimated values of the lattice constant and the bulk modulus at the two different energy cutoff. The comparison with other theoretical calculations [Satpathy (1986)] and experimental data shows a good agreement in the estimate of the lattice constant, while the bulk modulus is not completely satisfactory.

The analysis of fig.10 shows that the LDF formalism yields a correct description of the equilibrium crystal structure of CsBr. In fact it indicates without any doubt that the cesium chloride structure is stabler than the rocksalt.

High-Pressure Data

The study of the high pressure behaviour of the cesium bromide has presented remarkable difficulties, as explained before. Our calculations have been performed at different energy cutoffs to verify the stability of the shape of the total energy versus c/a ratio curves at several values of the volume ratio V/V_0, and only for $E_{pw} = 25Ry$ we have found a sufficient reduction of the numerical noise. For values of E_{pw} lower than 25 Ry, we don't find a converged behaviour of the total energy as a function of the lattice parameters.

Before performing more time-consuming calculations, accurate tests on the quality of the pseudopotentials and the energy-gap closure have been developed.

	a_0	B_0
$E_{pw}=21$ Ry	7.87	195
$E_{pw}=25$ Ry	8.00	176
Satpathy	8.14	169
exp.	8.24	143

Tab.3: Ceisum Bromide. Theoretical and Experimental Data.

Our final conclusions are: (1) the Kerker's pseudopotentials for both chemical species are satisfactory and no-discrepancies are found with the predictions derived whit differnt pseudopotentials. (2) At the investigated volume ratios ($V/V_0 \geq 0.48$) the energy-gap closure has not occurred.

The results of our calculations, performed with the higher energy cutoff, can be summarized as follows: at volume ratios greater than 0.53 only one minimum is observable (see fig.11.a) and it indicates clearly a stable cubic phase. For $V/V_0 = 0.52$ (see fig.11.b) the total energy curve is very flat in the interval $1.0 \leq c/a \leq 1.07$. This indicates the system may assume a tetragonal structure, because it has to step out a very low barrier which probably separates the two minima at the cubic and tetragonal phases. This hypothesis is confirmed by the curve at $V/V_0 = 0.51$, where an absolute minimum is observed at $c/a = 1.025$ (see fig.11.c).

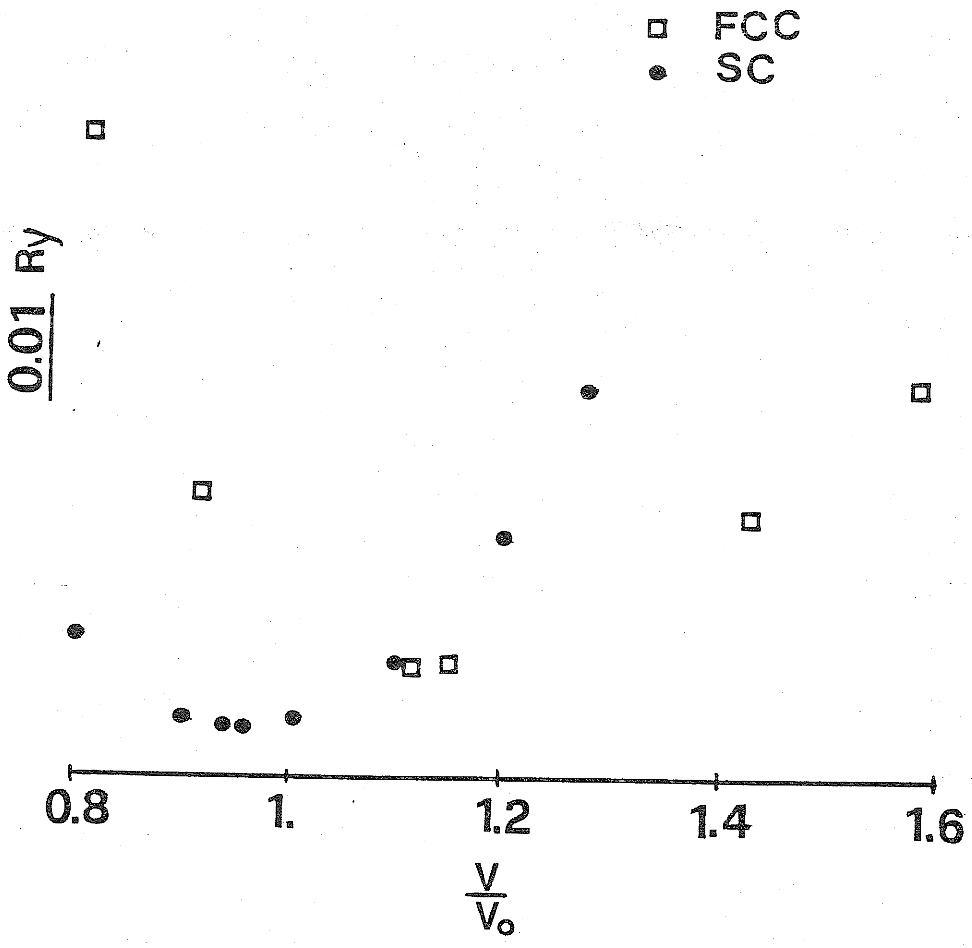


fig.10:Cesium Bromide. Lattice energy for the simple cubic phase (dots) and the rocksalt phase (squares) versus volume ratio

These results are in good agreement with the experimental observations, which indicate that the structural transition happens at $V/V_0 = 0.53 \pm 0.02$ in all cesium halides [Vohra, Duclos (1985)].

The underestimate of the c/a ratio at the transition is not very large (the experimental value is 1.08).

The predicted transition pressure is overstimated, the error is due to the overestimated value of the bulk modulus B_0 and is of the same order.

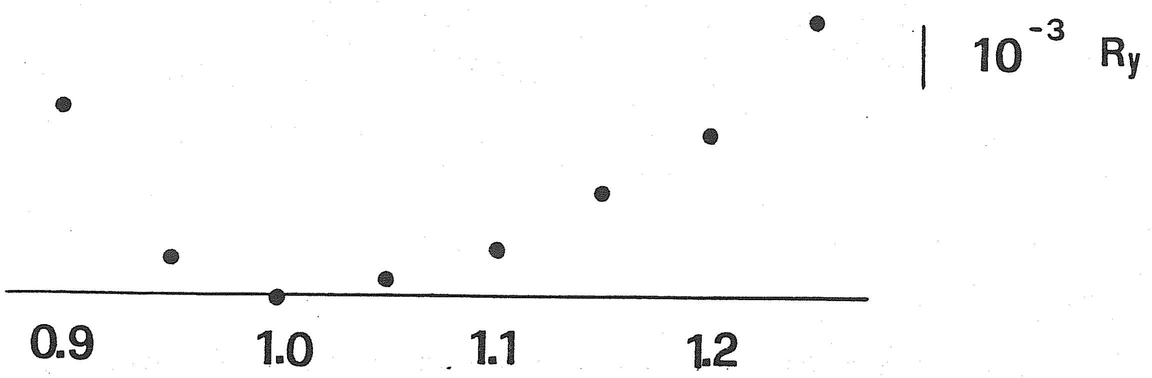


fig.11.a: CsBr Total energy versus c/a at $\frac{V}{V_0} = 0.54$

The degree of accurancy that we have achieved in the calculation of the total energy for this compounds, in view of the description of the tetragonal distortion, is very high: of the order of $\sim 10^{-4}$ *Ry*. It allows us to conclude that, without any doubt, our calculations show the occurence of the structural transition from the cubic to the tetragonal stucture, at a volume ratio in agree with the experimental data.

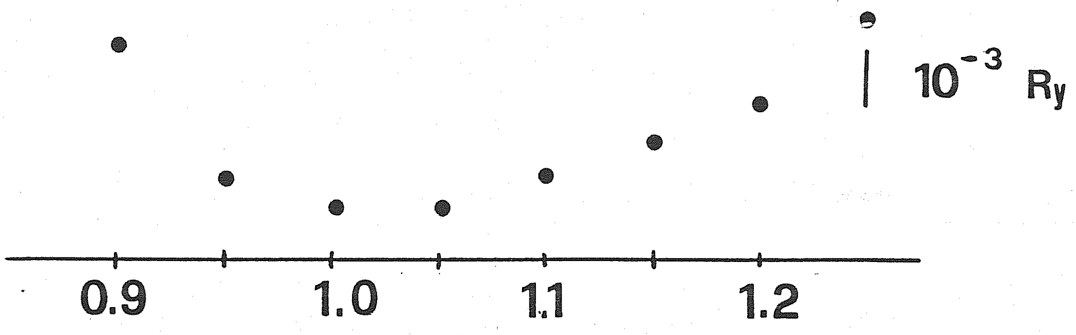


fig.11.b: CsBr Total energy versus c/a at $\frac{V}{V_0} = 0.52$

C.3.3) RUBIDIUM BROMIDE

Rubidium bromide is a salt that at equilibrium shows to be stable in the rocksalt structure and the experiments demonstrate that it undergoes the structural transition to a $B2$ structure at a very low pressure ($P_t = 5\ Kbar$). The

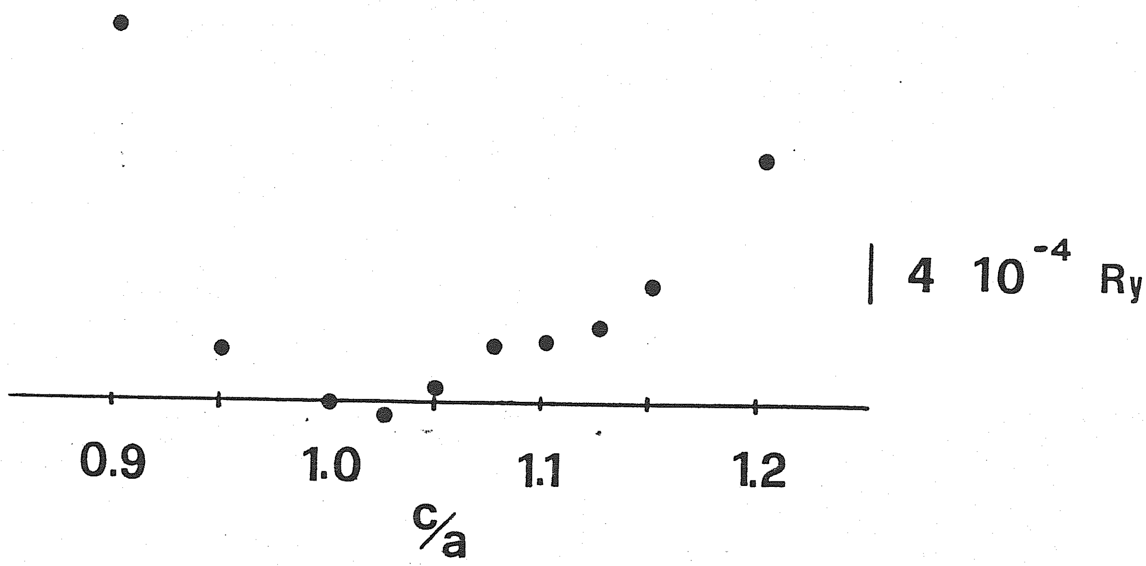


fig.11.c: CsBr Total energy versus c/a at $\frac{V}{V_0} = 0.51$

ab – initio pseudopotential LDF approach has been applied to the study of its zero-pressure properties. Its structural features (high compressibility and very moderate transition-pressure) have requested to achieve a very high numerical accurancy, in order to discriminate between two structural phases very close in energy.

In the present theoretical investigation we have obtained the behavior of the equilibrium parameters (lattice constant, bulk modulus and its first derivative respect to the pressure) versus the energy cutoff. Our results indicate that the theoretical predictions, for such very soft compound, converge slowly and request a very big computational effort.

A comparison of our results with experimental values is shown in tab.4 .

The agreement is satisfactory in view of the difficulties inherent in any fully *ab – initio* calculation of the equilibrium parameters of a highly compressible material like Rb-Br.

Our results indicate a very little difference between the energy minima calculated for rocksalt and cesium chloride structures (less than 0.1 mRy), see fig.12. Furthermore, this difference tends to vanish with increasing the energy cutoff of the calculation, indicating that the correct structural stability can be expected at very high cutoff (extremely large plane-wave basis set).

In conclusion, we can say our predictions indicate that the two structures are almost degenerate in energy, this is in good agreement with the experimental results which dysplay a very low transition pressure from the rocksalt structure to the B2 structure. The small discrepancy with the experimental results can be attributed to several motives, which are inherent to the present approach: inaccuracies in the exchange-correlation energy or in the pseudopotentials, intrinsical numerical noise.

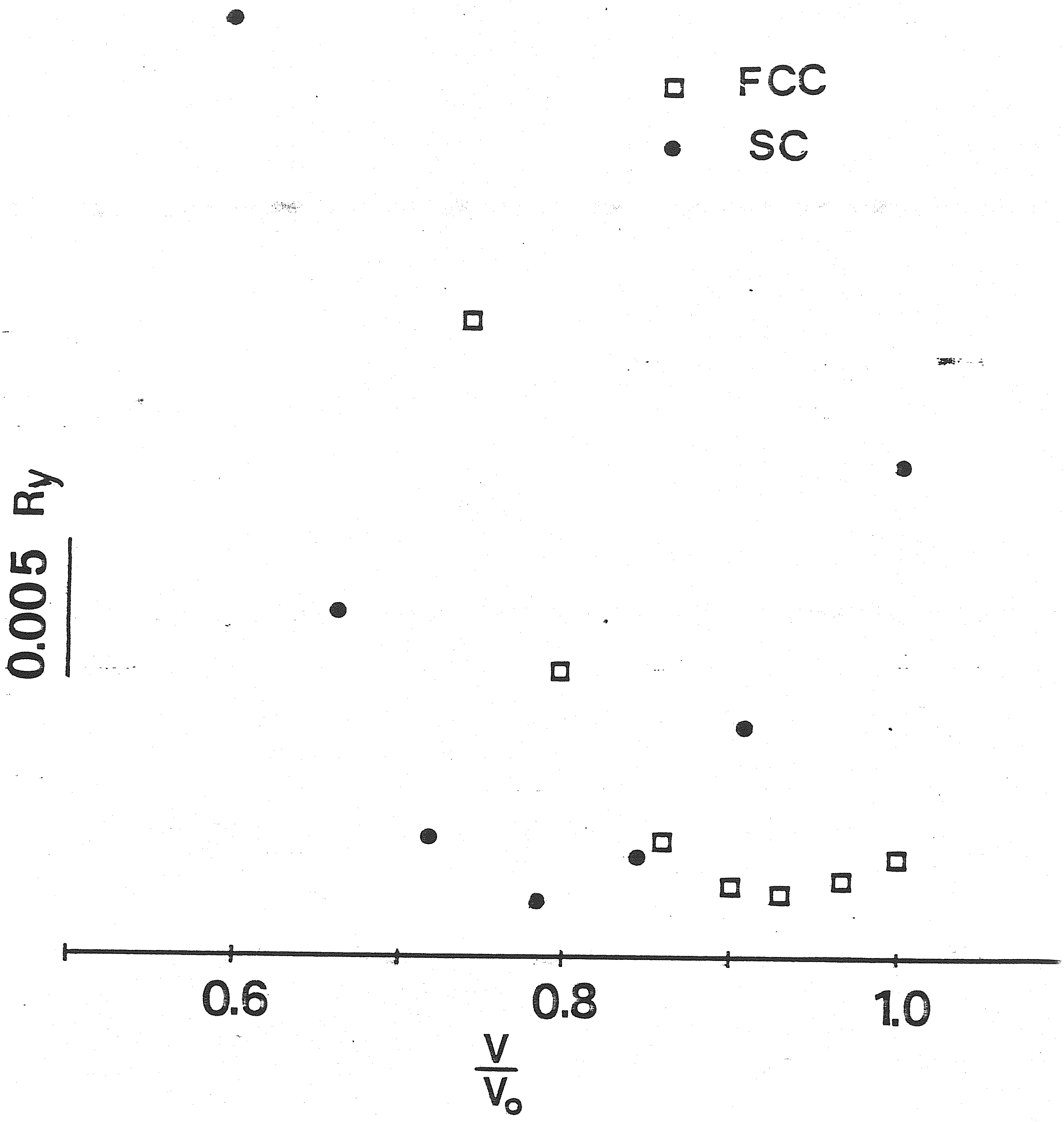


fig.12: Rubidium Bromide. Total energy for the rocksalt (squares) and the cesium-chloride (dots) structures

	a_0	B_0
exp.	12.945	130
theo.	12.63	159

tab.4 : Equilibrium parameters. Experimental and theoretical results for RbBr

CONCLUSIONS

In the course of this research we have studied the structural properties of some alkali halides by adopting model and *ab-initio* pseudopotential calculations. For the first time this latter technique has been applied to the study of the cesium bromide and rubidium bromide, allowing us to predict correctly many of their principal structural features.

Our model calculations have been performed by adopting a Born-like model, which have been recently proposed to study the structural instability of the cesium halides. Our calculations have displayed some serious deficiencies of this approach, which restrict its application to that part of the volume-pressure phase diagram on which the free parameters have been fitted to the experimental data. However, we must point out that such a model describes correctly the mechanism of the pressure-induced structural instability, observed in all the alkali halides, and which determines the distortion of the cubic structure into a tetragonal one.

The application of *ab-initio* calculations has permitted to study with great accurancy the structural properties of the cesium iodide, the cesium bromide and the rubidium bromide. We can summarize the results of these calculations in the following way: for the case of the cesium iodide, we have confirmed the results, recently obtained by Baroni and Giannozzi [Baroni, 1987], by using an higher numerical accurancy. This has permitted to verify and confirm the goodness of their results, and to point out better the great difficulties encountered in the study of such phenomena.

For the cesium bromide and rubidium bromide, this is the first study of their structural properties by an *ab-initio* technique. It has permitted to predict the structural instability of the cesium bromide under high pressure in good agreement with the experimental results. Also the zero pressure properties of this compound have been well described: the estimated lattice constant and the stable structure are quite in agreement with the experimental observations. In the case of the rubidium bromide the zero-pressure properties have been investigated. The application of this technique to such very soft system has requested a very big computational effort. The main goal of this study is the confirm of the very small difference in energy which separate the two observed structures of this compound, which performs a structural phase transition from the B1 lattice to the B2 lattice at a moderate pressure. Also the estimated values of the lattice constant and the bulk modulus are in satysfactory agreement with experimental results.

In conclusion we want to point out the importance of the adoption of an $ab-initio$ approach to the study of the structural properties of the ionic crystals, which is fundamental for a wide investigation of the phase diagram of these compounds. At the same time a non negligible computational effort is necessary, because the softness of these crystals requests to achieve a high numerical accurancy in order to discriminate between different structures which differ very little in energy.

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