



**ISAS - INTERNATIONAL SCHOOL  
FOR ADVANCED STUDIES**

**Phonon softening and low-symmetry  
phases of CsI at very high pressure:  
Landau theory and  
first-principles calculations.**

Thesis submitted for the degree of  
“Magister Philosophiæ”

CANDIDATE

Marco Buongiorno Nardelli

SUPERVISORS

Prof. Stefano Baroni

October 1991

**SISSA - SCUOLA  
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SUPERIORE  
DI STUDI AVANZATI**

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# Introduction

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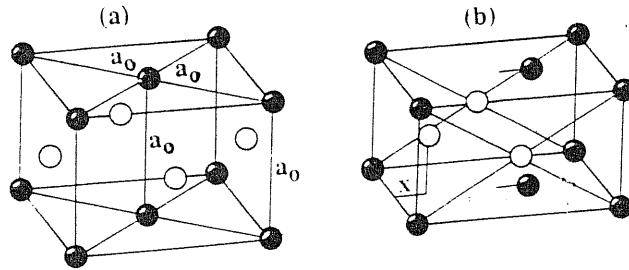
In recent years, the diamond-anvil cell technology has opened a major breakthrough in the physics of materials at very high pressures. One of the most striking features of solids at high pressure is the spontaneous lowering of the symmetry of some cubic compounds. Many experimental and theoretical investigations on CsI have been carried out, because of the wide variety of phenomena exhibited by this material on compression. Despite this, several inconsistencies still remain concerning its structural and electronic properties. In this work we will investigate from a theoretical point of view the structural phase transition that CsI undergoes at very high pressure ( hundreds of kilobars).

CsI is an ionic compound that crystalizes in the CsCl structure (simple cubic with basis: two atoms in  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  - space group  $O_h^1$ ). The first systematic studies of CsI under pressure date back to 1984. From X-ray diffraction experiments<sup>[1-4]</sup> it appeared that CsI undergoes a transition which lowers the cubic symmetry of the system at a pressure of  $39 \pm 1$  GPa corresponding at a volume  $V/V_0 = 0.544 \pm 0.003$  where  $V_0$  is the equilibrium volume. This transition is not peculiar to CsI only and has also been observed in other cesium halides. Further experiments on CsBr and CsCl showed a similar behaviour at  $53 \pm 2$  GPa ( $V/V_0 = 0.546 \pm 0.003$ ) and  $65 \pm 5$  GPa ( $V/V_0 = 0.53 \pm 0.02$ ) respectively. The common accepted picture of this transition was that a cubic-to- tetragonal deformation would occur. Group theory analysis within the Landau theory of phase transitions, unambiguously shows that this deformation

corresponds to a martensitic first order transition<sup>[28]</sup>. This is clearly confirmed by several independent calculations which indicate that the  $c/a$  ratio jumps discontinuously to  $c/a \approx 1.1 \div 1.2$  at the transition volume  $V/V_0 \approx 0.52 \div 0.54$  and increases continuously above the transition pressure. This discontinuity in  $c/a$  implies a discontinuity of the energy gap of about 0.3 eV, and of the pressure of about 20 kbar. This picture seems to be in contradiction with the experimental observations: no volume change is observed across the transition and the energy gap is continuous. These results would suggest that the transition is second order. Although the experimental values of  $c/a$  don't allow to exclude a first order transition, it seems that the lowest value of  $c/a$  observed is much lower than the values predicted by the theory. Some studies<sup>[2]</sup> also report a further transition from the tetragonal to the orthorhombic structure at about 56 GPa in CsI.

In 1989 Mao *et al.*<sup>[8-9]</sup> enriched the phenomenology of the structural phase transitions in CsI. They performed new energy-dispersive X-ray diffraction experiments. In their experiments they observed a continuous distortion of the CsI cell from the cubic to the orthorhombic structure. The observed distortion is continuous upon increasing pressure after the transition, and yield to a hexagonal-close-packet (hcp) structure above 200 GPa. Such a distortion is associated to the gliding of the (110) plane of the original cubic cell, as shown in Fig. 1. The starting point of the transition is observed at pressures as low as 15 GPa; however an unambiguous identification of the diffraction peaks corresponding to the orthorhombic structure can be obtained only around 45 GPa. The symmetry of the diffraction pattern clearly indicates that the gliding of the (110) plane could be due to the softening of a zone-edge phonon. This phonon should be the order parameter of a hypothetical second order phase transition. The hypothetical martensitic transition, even though first order, is characterized by a softening of the shear constant

$c_s = \frac{1}{2}(c_{11} - c_{12})$ , which is the second degree coefficient of the energy expansion in powers of  $c/a$ .  $c_s$  has been calculated to vanish slightly above the transition pressure, at a volume  $V/V_0 \approx 0.50$ . The link between the vanishing of the shear constant and the possible softening of a phonon mode is that  $c_s$  is one of the three sound velocity along the (110) direction<sup>[18]</sup>. Its vanishing could be then associated to the softening of the corresponding phonon mode. The two different hypothesis, the first order martensitic transition and the second order phonon driven one, are in competition in explaining the observed phenomena. In order to clarify these inconsistencies, we have performed a complete first principle study, including calculations of total energy, stress, and phonon frequencies. A complete and coherent picture of our results has been deduced in terms of the Landau Theory of phase transitions. Through this analysis we have obtained a clear characterization of the structural phase transition.



**Fig. 1:** Nature of the phase transition in CsI, as found in the experiments by Mao et al. . Panel a - the original cubic cell; panel b - an orthorhombic intermediate structure, showing also the gliding of the cubic (110) plane (from Ref. [8]). Solid spheres - Cs, empty spheres - I;  $a_0$  is the lattice parameter for the original cubic cell.



## Previous results.

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In order to understand the observed phase transition, many theoretical investigations have been done, both with models <sup>[5]</sup> and from first principles <sup>[6,7]</sup>. The transition was studied for the first time by Vohra *et al* <sup>[5]</sup> using a Born-Mayer expression for modelling the interionic interaction. This model was able to describe the transition with a reasonable degree of accuracy: they confirmed the first order character of the cubic-to-tetragonal transition, studying the discontinuous increase of  $c/a$  at the transition pressure; they explained it in terms of the competition between the electrostatic and repulsive interactions; they found that the shear constant is still positive at the transition volume. However the parameters chosen to describe the high pressure phase, predict an incorrect rocksalt structure for the zero pressure phase. This is a common characteristic of calculations based on empirical model: they have a limited predictive power. In fact, the parameters entering this model are fitted to the experiments performed at very high pressure, and are unable to predict behaviours different from those experimentally observed.

First principle calculations have been performed by Christensen *et al.* <sup>[6]</sup> in the framework of the atomic sphere approximation linear muffin tin orbitals (ASA-LMTO) method. They explored in detail the behaviour of the system around the cubic-to-tetragonal phase transition, globally confirming the previous picture from the empirical model. Studying the dependence of the gap upon pressure, they were also able to

predict that metallization would occur at  $V/V_0 \approx 0.5$ . This calculations - though very accurate in many respects - suffered from the use of the atomic sphere approximation, an approximate way to treat the deviations of the crystal charge density from the superposition of spherical muffin tin ionic distributions.

A self-consistent *ab-initio* study without any assumption on the shape of the electronic charge density has been performed by S. Baroni and P. Giannozzi <sup>[7]</sup> using norm-conserving pseudopotentials. They have confirmed the previous characterizations of the transition; moreover they observed a discontinuity of about 0.3 eV in the optical gap for  $c/a = 1.0$  to  $c/a = 1.15$  at the transition point. This discontinuity is in perfect agreement with the first order character of the transition, but is contrary to previous optical measurement.

Up to 1989 the theoretical studies were in fearely good agreement in explaining the cubic-to-tetragonal transition, but the picture was not lacking of inconsistencies between experimental and theoretical results. In 1989, the experiments performed by Mao *et al.* renewed the interest in the phenomena exhibited by CsI upon very high pressure. As stated before, they observed a continuous distortion of the CsI cell from the cubic to the orthorhombic structure. The most striking feature observed in the X-ray diffraction spectra is associated to the splitting of the 110 peak into a quintuplet after the transition. The components of the quintuplet can be assigned as follows: a triplet (020, 002, 111) related to the new orthorhombic cell, and a doublet (110, 021) to the gliding of the (110) plane. The observed splitting and intensities of the peaks evolve continuously from 15 to 100 GPa, showing a single orthorhombic phase with variable parameters; even though the experiments seem to show a continuous distortion from the cubic to the orthorhombic cell, a weak first order character of the transition cannot

be ruled out. Starting from these results we decided to perform a deeper investigation of such a transition, using first principle techniques.

## Method

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Our calculations have been performed in the framework of a combined approach based on density functional and linear response theory to obtain total energies, forces, stresses and phonon frequencies for various volumes and different crystal structures. The self-consistent calculations have been performed within the Local Density Approximation (LDA) using norm-conserving pseudopotentials and large plane wave basis set [10]. For each crystal structure and microscopic arrangement of ions, we computed the forces acting on the atoms using the Hellmann-Feynman theorem [14], and the macroscopic stresses, along the lines suggested by Nilsen and Martin [15]. Phonon dispersion have been calculated using Density Functional perturbation theory [12] which allows one to compute dynamical matrices at arbitrary wave vector with a computational effort comparable to that of a self consistent calculation for the unperturbed crystal. Recently this method has been successfully applied to the calculation of phonon dispersion relations in semiconductors [13].

All the calculations have been performed using a set of  $k$  points in the irreducible wedge of the first Brillouin zone corresponding to the meshes of 4, 10 or 20 points for the simple cubic structure in the Monkhorst and Pack scheme [10]. We generated pseudopotentials for Cs and I using the Kerker's procedure [11], including angular momenta up to  $l = 3$ ; we included in the core Cs 5s and 5p orbitals, as discussed in Ref. 7. Plane waves corresponding to a 25 Ryd cut-off were included in the basis set. We have tested

the convergency of total energies, stresses, and phonon dispersion both in the number of special points and of the plane wave basis set used (up to 40 Ryd cut-off). Even though total energies are not fully converged at a cut-off as high as 40 Ryd, we have verified that all the other meaningful structural and dynamical quantity are well converged with a 25 Ryd cut-off.

# Structural and dynamical properties of CsI under pressure

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## *Zero - pressure properties*

We have computed the equation of state of CsI fitting total energies and pressures to the isothermal equation of state of Rose <sup>[16]</sup> :

$$P(V) = 3B_0 \frac{1-X}{X^2} e^{\eta(1-X)}$$

$$X = (V/V_0)^{1/3} \quad \text{and} \quad \eta = \frac{1}{2}(3B'_0 - 1)$$

and Murnaghan <sup>[17]</sup>:

$$P(V) = \frac{B_0}{B'_0} (X^{-3B'_0} - 1).$$

The results are summarized in the following table. The theoretical values are referred to a calculation performed with 4 k points and a 25 Ryd cut-off. In parenthesis are indicated, for comparison, the values obtained with a 40 Ryd cut-off.

	Rose	Murnaghan	Exp. [8]
$a_0(\text{\AA})$	4.430 (4.435)	4.439 (4.434)	4.568
$B_0(\text{GPa})$	15.2 (16.0)	15.4 (16.6)	$13.5 \pm 0.2$
$B'_0$	5.64 (5.51)	3.84 (5.43)	$5.45 \pm 0.06$

The agreement with the experimental data is quite satisfactory. In Fig. 2 we compare the Rose equation of state as fitted to theoretical calculations and to experiments.

### *Structure and dynamics under pressure*

As anticipated before, the main idea of this study is that the transition could be driven by a phonon mode whose frequency would soften upon increasing pressure. The gliding of the (110) plane observed experimentally can be viewed as a phonon mode for  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ , the M point at the edge of the first Brillouin zone of the cubic structure. Such a mode along (110) could be responsible for the transition, as indicated by the fact that the shear constant  $c_s = \frac{1}{2}(c_{11} - c_{12})$ , that vanishes not far above the transition pressure, is actually one of the three sound velocities along the (110) direction. This behaviour is common to a variety of systems that undergo pressure induced phase transitions<sup>[19]</sup>. An example is the Paratellurite ( $\text{TeO}_2$ ) that undergoes a pressure induced, soft-phonon driven phase transition from the tetragonal to the orthorhombic structure<sup>[20]</sup>.

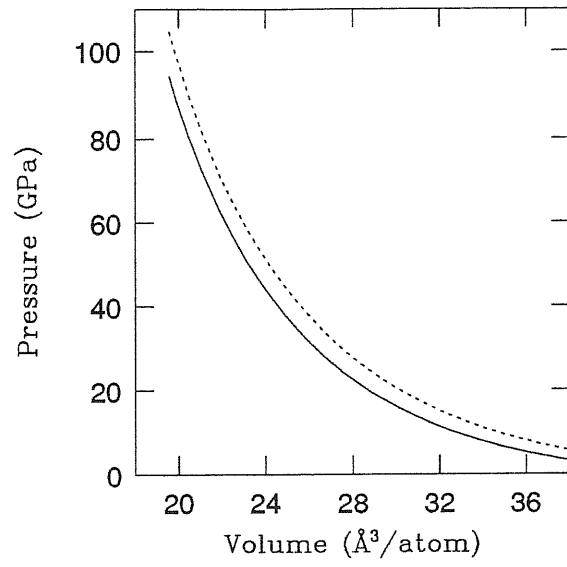
Following this approach, we have studied the behaviour of the zone edge phonon frequency vs. compression. The phonon responsible for the phase transition is the doubly degenerate acoustic mode in M. In Fig. 3a we display the phonon dispersion of CsI calculated along the (110) at equilibrium volume. In the picture are also indicated the experimental values for the two modes we are interested in<sup>[29]</sup>. In Fig. 3b we report the detail of the acoustic branches just above and below the critical volume ( $V/V_0 = 0.638$ ) at which the frequency of the doubly degenerate mode in M vanishes. These results allow us to identify the amplitude of this mode as the order parameter  $\gamma$  of a second order phase transition in the Landau sense. The dimensionality of this order parameter

is easily obtained, considering the fact that the star of M is formed by three vectors. For each of them there are two modes, and then the order parameter is six-dimensional,  $\gamma = (\gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5, \gamma_6)$ . Each component corresponds to a pattern displacement following the auto-displacement of a zone edge phonon for  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0); (\frac{1}{2}, 0, \frac{1}{2}); (0, \frac{1}{2}, \frac{1}{2})$ .

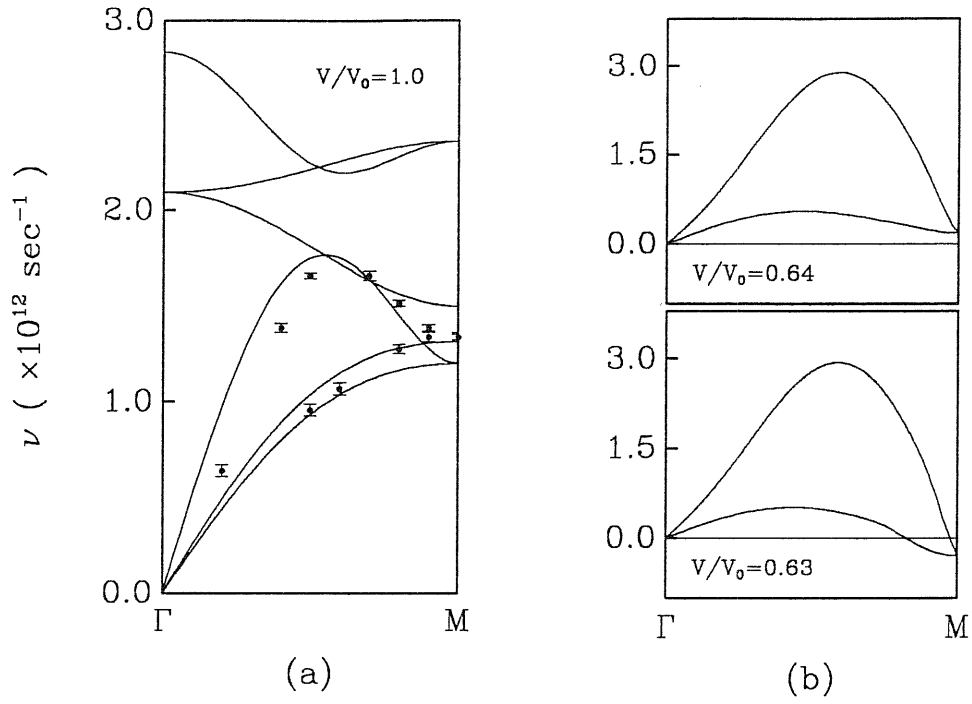
In Fig. 4 we show the dependence of the zone edge frequency vs. compression. The frequency vanishes for  $V/V_0 = 0.638$  at a critical pressure  $P_c = 22.9$  GPa. Note that these calculated volume and pressure are respectively well above and below those previously calculated for the martensitic cubic-to-tetragonal transition ( $V/V_0 = 0.54$   $P \approx 45$  GPa).

Both the auto-displacements in M actually correspond to the gliding of the (110) plane (and its orthogonal ( $1\bar{1}0$ )), but with different displacement length for Cs and I atoms, where the latter has a length that is about 0.9 the one of the former. In order to inquire all the possible stable phases that can be induced by these phonons, we have analyzed the transition in the framework of the Landau theory of phase transition, that is the common tool to perform this kind of analysis.

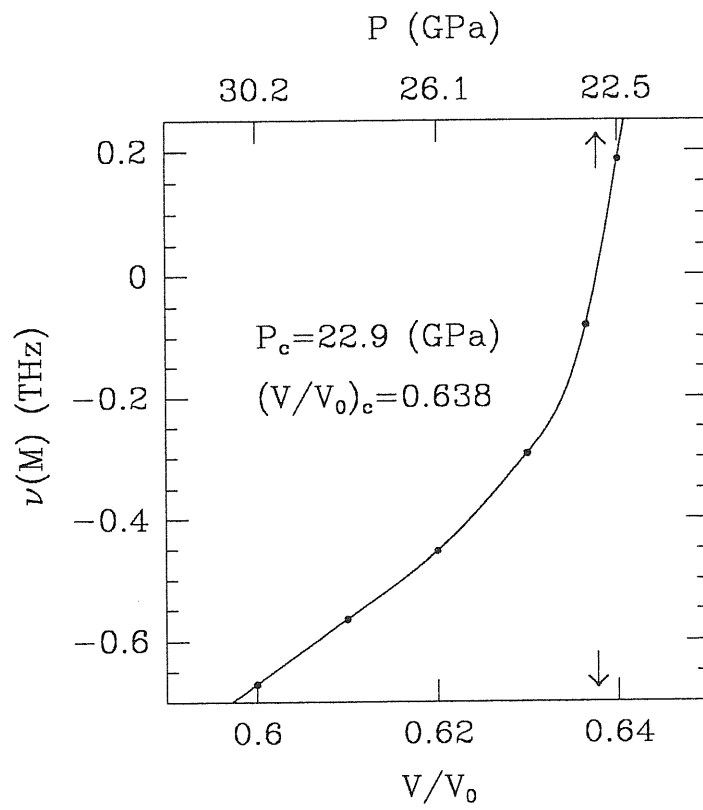




**Fig. 2:** Comparison between the experimental and calculated (Rose) equations of state; solid line: theory, dotted line: experiment.



**Fig. 3:** Panel (a): dispersion relations at equilibrium. Experimental data are shown for the two modes we are interested in (from Ref. 29); the theory refers to a calculation with 4 special points and a 20 Ryd cut-off; Panel (b): dispersion relations for the two modes whose frequency soften at the M point of the first Brillouin zone for two different volumes. Negative values corresponds to imaginary frequencies.



**Fig. 4:** Zone edge phonon frequency vs. volume and pressure. Transition volume and pressure are indicated by arrows. Negative frequencies mean imaginary values.

## Theoretical analysis of the phase transformation

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A general phenomenological theory for continuous phase transitions, based on symmetry arguments, has been given by Landau<sup>[21]</sup>. This theory lies on the hypothesis that the free energy of the system at the transition can be expanded in a power series of a quantity called “order parameter”. The characteristics of the order parameter are that it is zero in the more symmetric phase (above the transition), and different from zero in the less symmetric one (in the following we will call symmetric the more symmetric phase). The transition being continuous, the order parameter,  $\gamma$ , will assume infinitesimal values around the transition point. Assuming that the free energy is analytical around the transition, its power series given by

$$\mathcal{E}(V, \gamma) = F_0 + \alpha\gamma + A(V)\gamma^2 + C(V)\gamma^3 + B(V)\gamma^4 + \dots \quad (1)$$

If the states for  $\gamma = 0$  and  $\gamma \neq 0$  are distinguishable for their symmetry, the first order term must be identically zero. The second order term must be zero at the transition point but  $> 0$  in the more symmetric phase and  $< 0$  in the less symmetric one. In order to have a stable transition point, (*i.e.*  $F$  minimum for  $\gamma = 0$ ) also the third order term must be zero at the transition, and the fourth order one must be positive. A second order phase transition is characterized by the fact that  $C(V) \equiv 0$  identically.

It is possible to classify the symmetry change that can occur at the transition with the following procedure<sup>[22]</sup> :

(1) *Find the order parameter associated with the transition.*

In our case, the order parameter is the displacement pattern of the atoms in the cell, corresponding to the soft phonon modes. The order parameters transform into each other upon a symmetry operation of the symmetric phase as partners of an irreducible representation of its symmetry group.

(2) *Find the space group of the high symmetry phase of the system, and the irreducible representation induced by the order parameter  $\gamma$ .*

For the transition to be second order, this irreducible representation should comply with the Landau and Lifshitz condition for a continuous commensurate phase transition. This condition can be formulated also by saying that the symmetric cube of the irreducible representation of the order parameter does not contain the identical representation, *i.e.* the only linear combinations of monomials of the form  $\gamma_i\gamma_j\gamma_k$  which is invariant under all the symmetry operations of the symmetric phase is the null polynomial.

In our system the space group of the high symmetry phase is  $O_h^1$ ; the order parameter of the transition is the displacement pattern induced by the phonons in M. To find the irreducible representation associated to these modes we have to classify the normal modes for that specific point of the first Brillouin zone. Given the point group of the M point,  $D_{4h}$ , we found that the modes we are studying transform like the antisymmetric bidimensional representation  $\Gamma_5^-$  (in the following we use the notation of Ref. 22 for the groups and the irreducible representations). First of all, we easily verify that the Landau and Lifshitz condition is complied, because, being the irreducible representation odd with respect to parity, its cube will necessarily be odd and hence not invariant.

(3) *Find the set of basic invariant polynomials in  $\gamma$  up to degree four, which enter the*

free energy expansion, eq. (1).

These polynomials can be obtained using standard techniques of group theory<sup>[24,25]</sup>, but we used the following simpler procedure. First of all, we know that the number of fourth order invariant is equal to four, because the identical representation is contained four times in the 4-th symmetric power of the irreducible representation. A way to obtain them is to operate on the possible fourth power combinations of  $\gamma$ 's with all the symmetry operations of the point group of the more symmetric phase. The starting combination must obey some symmetry conditions: given  $\gamma_i\gamma_j\gamma_k\gamma_l$ , one must have  $\mathbf{k}_i + \mathbf{k}_j + \mathbf{k}_l + \mathbf{k}_k = \mathbf{G}$ , where  $\mathbf{k}_i$  is the particular  $\mathbf{k}$  vector corresponding to the particular phonon  $\gamma_i$ , and  $\mathbf{G}$  is a reciprocal space vector. This is due to the invariance of the system under rigid translations, and it implies that the two phonons associated to the same  $\mathbf{k}$  vector of the star must be always coupled. The basic invariants are summarized in the following table:

starting combination	invariant
$\gamma_1\gamma_1\gamma_1\gamma_1$	$\gamma_1^4 + \gamma_2^4 + \gamma_3^4 + \gamma_4^4 + \gamma_5^4 + \gamma_6^4$
$\gamma_1\gamma_1\gamma_2\gamma_2$	$\gamma_1^2\gamma_2^2 + \gamma_3^2\gamma_4^2 + \gamma_5^2\gamma_6^2$
$\gamma_1\gamma_2\gamma_3\gamma_3$	$-\gamma_1\gamma_2(\gamma_3^2 + \gamma_4^2 - \gamma_5^2 - \gamma_6^2) +$ $\gamma_3\gamma_4(\gamma_5^2 + \gamma_6^2 - \gamma_1^2 - \gamma_2^2) +$ $\gamma_5\gamma_6(\gamma_1^2 + \gamma_2^2 - \gamma_3^2 - \gamma_4^2)$
$\gamma_1\gamma_2\gamma_3\gamma_4$	$-\gamma_1\gamma_2\gamma_3\gamma_4 - \gamma_1\gamma_2\gamma_5\gamma_6 + \gamma_3\gamma_4\gamma_5\gamma_6$

(4) Minimize the Landau potential consisting of the basis set of invariant and find the  $\gamma_0$  corresponding to the absolute minimum.

This is, by far, the most difficult problem to solve in order to get sensible results from

the Landau approach, but it is also much studied by group theorists<sup>[24–27]</sup>. For our specific case, we refer to Ref. 24, where a complete description of the six-dimensional order parameter case is carried out. Following the notation of Ref. 24, the possible stable phases can be classified as follows:

	direction	symmetry group
P1	(a, 0,0, 0,0, 0)	$D_{2h}^5$
P2	(a,-a,0, 0,0, 0)	$D_{2h}^{19}$
P6	(a, 0,a, 0,a, 0)	$C_{3v}^5$
P7	(0,-a,0, a,0, a)	$D_3^7$
P9	(a,-a,a,-a,0, 0)	$D_{4h}^{17}$
P10	(a,-a,0, 0,a,-a)	$D_{4h}^{17}$
P11	(a,-a,a, a,a, a)	$T^5$

where each configuration corresponds to a particular direction in the order parameter space, *i.e.* to a particular combination of phonon displacements. We have verified that for each direction there was an energy minimum and for each case we determined the corresponding length of the displacement. In Fig. 5 the two energy minima along P1 and P2 are shown.

Once we have determined the symmetry of the possible stable phases, we have to inquire for a coupling between phonon displacements and continuous deformation of the unit cell, *i.e.*, we have to take into account the elastic deformation that the soft phonon can induce in the system. To consider the coupling between phonons and elastic deformation of the cell, we have to construct all the possible invariants of the kind  $\gamma^2 \epsilon$ , where  $\epsilon$  are the strain components. These are the only fourth order terms that survive in

the free energy expansion (for a demonstration see the Appendix). In the Appendix the method to construct these invariants is also discussed in detail, and the four invariants that can be constructed are:

$$\begin{aligned} & \frac{1}{3}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})(\gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2) \\ & (2(\gamma_1^2 + \gamma_2^2) - \gamma_3^2 - \gamma_4^2 - \gamma_5^2 - \gamma_6^2)(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) + 3(\gamma_3^2 + \gamma_4^2 - \gamma_5^2 - \gamma_6^2)(\epsilon_{xx} - \epsilon_{yy}) \\ & (-2\gamma_1\gamma_2 - \gamma_3\gamma_4 - \gamma_5\gamma_6)(\epsilon_{xx} - \epsilon_{yy}) + (-\gamma_3\gamma_4 + \gamma_5\gamma_6)(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) \\ & (\gamma_1^2 - \gamma_2^2)\epsilon_{xy} + (\gamma_3^2 - \gamma_4^2)\epsilon_{yz} + (\gamma_5^2 - \gamma_6^2)\epsilon_{xz} \end{aligned}$$

Moreover also the pure elastic energy terms must be included in the free energy expansion. For a cubic crystal this reads:

$$\begin{aligned} & \frac{1}{2}C_{11}(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + C_{12}(\epsilon_{xx}\epsilon_{yy} + \epsilon_{xx}\epsilon_{zz} + \epsilon_{yy}\epsilon_{zz}) + \\ & \frac{1}{2}C_{44}(\epsilon_{xy}^2 + \epsilon_{xz}^2 + \epsilon_{yz}^2) - P_0\Omega_{cell}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \end{aligned}$$

where  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  are the three independent elastic constants, and the last linear term takes into account the external pressure for each volume.

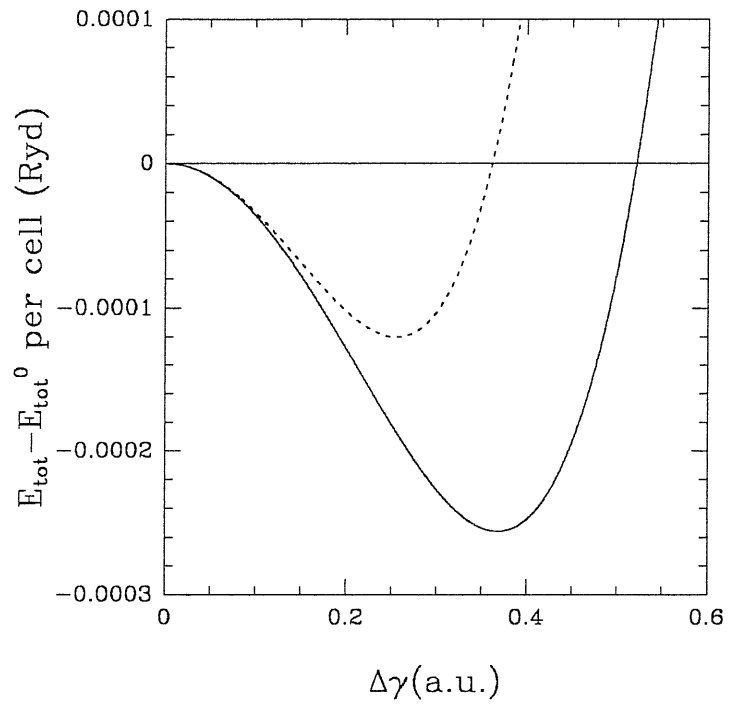
At the end, the complete expression of the Landau free energy per cell, including the phonon - strain coupling is given by :

$$\begin{aligned} \mathcal{E} = & \mathcal{A} (\gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2) + \\ & \mathcal{A}' (\gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2)^2 + \\ & \mathcal{B}_1 (\gamma_1^4 + \gamma_2^4 + \gamma_3^4 + \gamma_4^4 + \gamma_5^4 + \gamma_6^4) + \\ & \mathcal{B}_2 (\gamma_1^2\gamma_2^2 + \gamma_3^2\gamma_4^2 + \gamma_5^2\gamma_6^2) + \\ & \mathcal{B}_6 [-\gamma_1\gamma_2(\gamma_3^2 + \gamma_4^2 - \gamma_5^2 - \gamma_6^2) + \gamma_3\gamma_4(\gamma_5^2 + \gamma_6^2 - \gamma_1^2 - \gamma_2^2) + \gamma_5\gamma_6(\gamma_1^2 + \gamma_2^2 - \gamma_3^2 - \gamma_4^2)] + \end{aligned}$$



$$\begin{aligned}
& \mathcal{B}_3 (-\gamma_1\gamma_2\gamma_3\gamma_4 - \gamma_1\gamma_2\gamma_5\gamma_6 + \gamma_3\gamma_4\gamma_5\gamma_6) + \\
& C_1 \frac{1}{3}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})(\gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2) + \\
& C_2 [(2(\gamma_1^2 + \gamma_2^2) - \gamma_3^2 - \gamma_4^2 - \gamma_5^2 - \gamma_6^2)(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) + 3(\gamma_3^2 + \gamma_4^2 - \gamma_5^2 - \gamma_6^2)(\epsilon_{xx} - \epsilon_{yy})] + \\
& C_3 [(-2\gamma_1\gamma_2 - \gamma_3\gamma_4 - \gamma_5\gamma_6)(\epsilon_{xx} - \epsilon_{yy}) + (-\gamma_3\gamma_4 + \gamma_5\gamma_6)(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})] + \\
& C_4 [(\gamma_1^2 - \gamma_2^2)\epsilon_{xy} + (\gamma_3^2 - \gamma_4^2)\epsilon_{yz} + (\gamma_5^2 - \gamma_6^2)\epsilon_{xz}] + \\
& C_{11} \frac{1}{2}(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + \\
& C_{12} (\epsilon_{xx}\epsilon_{yy} + \epsilon_{xx}\epsilon_{zz} + \epsilon_{yy}\epsilon_{zz}) + \\
& C_{44} \frac{1}{2}(\epsilon_{xy}^2 + \epsilon_{xz}^2 + \epsilon_{yz}^2) - \\
& P_0 \Omega_{cell}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \tag{2}
\end{aligned}$$

The problem at this point is to calculate the coefficients of this expansion by means of first principle techniques.



**Fig. 5:** Energy vs. phonon displacement length along two particular direction of the order parameter space; continuous line: along P1, dotted line: along P2

## Ab-initio determination of the free-energy coefficients.

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All the coefficients in the free energy have been computed by means of fitting procedures both on total energy and stress calculations. All the data have been collected in the following table for two different  $V/V_0$  ratios below the transition point:

	$V/V_0 = 0.58$	$V/V_0 = 0.50$
$A$	-0.00378	-0.01185
$A'$	0.02011	0.05369
$B_1$	-0.00621	-0.03339
$B_2$	0.04558	0.05718
$B_6$	0.04082	0.03638
$B_3$	-0.17560	-0.46068
$C_1$	0.00007	-0.00003
$C_2$	0.02570	0.04330
$C_3$	0.02996	-0.03580
$C_4$	-0.09320	-0.26580
$C_{11}$	6.524	8.240
$C_{12}$	6.431	8.322
$C_{44}$	6.332	-

All the calculations used for the fitting have been performed with a plane wave cut-off of 25 Ryd and the equivalent of 10 k points in the irreducible wedge of the first Brillouin zone for the cubic unit cell. The parameters from  $\mathcal{A}$  to  $\mathcal{B}_6$  have been obtained fitting total energy calculations for different atomic displacements following a particular direction in the order parameter space, without strain of the cell; the others through stress calculations, knowing that, by definition:

$$\sigma_{ij} = -\frac{1}{\Omega_{cell}} \frac{\partial \mathcal{E}}{\partial \epsilon_{ij}}.$$

Note that the values of the elastic constants  $C_{11}$  and  $C_{12}$  give the value of the shear constant  $c_s$ , and that  $c_s$  is negative at  $V/V_0 = 0.50$  in agreement with all the previous calculations.

## Study of the stable phases.

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Once the coefficients of the free energy expansion have been determined, we performed a complete study of the stability of the free energy along the minimal directions of maximal isotropy in the order parameter space. To study the stability we determined the location of the minima along the various directions and we analyzed the nature of the singular point (minimum, maximum or saddle) by looking at the sign of the hessian matrix.

Without the inclusion in the free energy of the phonon-strain coupling, the only configuration that corresponds to a minimum is associated to the P11 direction, *i.e.* the system would enlarge its cell four times and maintain a cubic symmetry (space group  $T_5$ ). Such a symmetry however would not explain the evolution of the (110) peak as seen in the X-ray diffraction experiments. The inclusion of the phonon-strain coupling turns out to drastically change this picture.

In fact, the role of the new terms is to renormalize the fourth order coefficients in the free energy expansion. If we take the expression of the free energy along a certain direction (see Appendix)

$$\mathcal{E} = -\omega^2\gamma^2 + I\gamma^4 + \Lambda\epsilon^2 + A\gamma^2\epsilon$$

and apply the equilibrium condition

$$\frac{\partial\mathcal{E}}{\partial\epsilon} = 0$$

we obtain

$$\epsilon = -\frac{1}{2}\Lambda^{-1}A\gamma^2.$$

Substituting in  $\mathcal{E}$ , we have

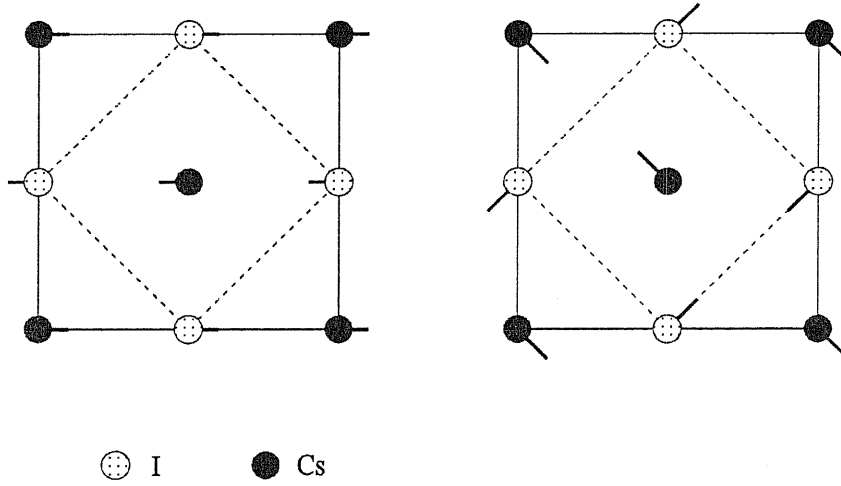
$$\mathcal{E}_{min} = -\omega^2\gamma^2 + \left(I - \frac{1}{2}A\Lambda^{-1}A\right)\gamma^4$$

where the fourth order coefficient  $I$ , has been renormalized by the phonon - strain coupling. This new coefficient doesn't change much the behaviour of the system along the directions from P6 to P10, even if the energy saddles are more pronounced; it doesn't change at all the behaviour along P11, because the system is not coupled to the strain, due to the fact that the cubic symmetry is preserved.

Along P1 and P2 the behaviour is completely different, because the strain coupling is so strong that the fourth order renormalized coefficient becomes negative. This means that along P1 and P2 there are much stronger minima than in other directions, and that the Landau expansion is instable along such directions. To treat the problem along the lines the Landau theory, we should include in the free energy expansion the sixth order terms. At this point, however, we already have all the informations we need to perform a numerical minimization procedure to get the equilibrium configuration after the transition. The results of this numerical minimization are summarized in the following table for  $V/V_0 = 0.58$ , and in Fig. 6 the two phonon pattern along P1 and P2 are shown:

Direction	$\gamma_{min}$ (a.u.)	$\mathcal{E}_{min}$ (mRyd)	$\gamma_{min}$ (a.u.)	$\mathcal{E}_{min}$ (mRyd)
	(no strain)	(no strain)	(strain)	(strain)
P1	0.368	-0.256	0.631	-1.384
P2	0.182	-0.125	in progress	in progress
P6	0.187	-0.197	0.188	-0.200
P7	0.187	-0.197	0.188	-0.200
P9	0.102	-0.078	0.158	-0.189
P10	0.137	-0.142	0.143	-0.154
P11	0.195	-0.432	0.195	-0.432

Even though the calculations for the P2 direction are still in progress, we expect that the gain in energy will be less than along P1. Without the inclusion of the strain in the free energy, the value of the minimum along P1 was nearly one half than the minimum along P2. We expect that this difference between the two minima will be conserved. The fact that the P1 structure seems to be the most stable one is in perfect agreement with the X-ray diffraction experiments, and explains in detail the mechanism of the phase transition.



**Fig. 6:** Top view of the cubic unit cell (dashed) of CsI showing the two displacement pattern induced by the P1 (left) and P2 (right) phonon configuration.



## Conclusions

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In this work we have performed a complete first principle study of the high pressure phase transitions of CsI. This system undergoes a cubic to orthorhombic second order transition, driven by a shear acoustic mode at zone boundary along the (110) direction. Through a combined approach based on the Landau theory and first principle techniques we have been able to identify that the final structure just below the phase transition is orthorhombic, space group  $D_{2h}^5$ , with a displacement of the atoms on the original (110) plane in the cubic structure induced by the soft phonon mode. This picture is in agreement with the recent X-ray diffraction experiments.

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## Appendix

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Consider the generic expression of the Landau free energy projected along a certain direction of the order parameter space:

$$\mathcal{E} = -\omega^2\gamma^2 + I\gamma^4 + F[\gamma, \epsilon]$$

where  $\gamma^n$  stands for all the possible invariant combination of power n, and  $F[\gamma, \epsilon]$  is the term of phonon - strain coupling, containing all the possible products of the kind (up to the fourth order):

$$\epsilon^2, \gamma\epsilon, \gamma^2\epsilon, \gamma\epsilon^2, \gamma\epsilon^3, \gamma^2\epsilon^2, \gamma^3\epsilon$$

. All the products that contain an even power of  $\gamma$  are not invariant and so they cancel. The only products that remain are  $\epsilon^2$ , that is the elastic energy term,  $\gamma^2\epsilon$  and  $\gamma^2\epsilon^2$ . Up to fourth order only  $\gamma^2\epsilon$  must be considered; in fact we can easily demonstrate that  $\epsilon \approx \gamma^2$  and so  $\gamma^2\epsilon^2$  is actually of sixth order in the order parameter. To see this, starting from

$$\mathcal{E} = -\omega^2\gamma^2 + I\gamma^4 + \Lambda\epsilon^2 + \alpha\gamma^2\epsilon + \beta\gamma^2\epsilon^2$$

and from the equilibrium condition

$$\frac{\partial \mathcal{E}}{\partial \epsilon} = 0$$

we get

$$2\Lambda\epsilon + \alpha\gamma^2 + 2\beta\gamma^2\epsilon = 0$$

and so

$$\epsilon = \frac{1}{2} \frac{\alpha \gamma^2}{\Lambda + \beta \gamma^2} \approx \gamma^2$$

Q.E.D.

To find the form of the  $\gamma^2 \epsilon$  invariant we have followed this procedure.

We have determined all the second order products such that  $\mathbf{k}_i + \mathbf{k}_j = \mathbf{G}$ . These correspond to a 9-dimensional representation that can be decomposed in a 3-dimensional one

$$\gamma_1 \gamma_2, \gamma_3 \gamma_4, \gamma_5 \gamma_6$$

plus a 6-dimensional one

$$\gamma_1^2, \gamma_2^2, \gamma_3^2, \gamma_4^2, \gamma_5^2, \gamma_6^2.$$

These can be decomposed as:

$$6 - \text{dim} \rightarrow \Gamma_1 + \Gamma_3 + \Gamma_5$$

$$3 - \text{dim} \rightarrow \Gamma_2 + \Gamma_3.$$

Knowing that, we constructed the combinations of  $\gamma$ 's that correspond to the basis functions of the irreducible representations:

6-dimensional representation

$$\Gamma_1 \rightarrow \gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2$$

$$\Gamma_3 \rightarrow 2(\gamma_1^2 + \gamma_2^2) - \gamma_3^2 - \gamma_4^2 - \gamma_5^2 - \gamma_6^2$$

$$\gamma_3^2 + \gamma_4^2 - \gamma_5^2 - \gamma_6^2$$

$$\Gamma_5 \rightarrow \gamma_1^2 - \gamma_2^2; \gamma_3^2 - \gamma_4^2; \gamma_5^2 - \gamma_6^2$$

3-dimensional representation

$$\Gamma_2 \rightarrow -\gamma_1 \gamma_2 + \gamma_3 \gamma_4 + \gamma_5 \gamma_6$$

$$\Gamma_3 \rightarrow -2\gamma_1 \gamma_2 - \gamma_3 \gamma_4 - \gamma_5 \gamma_6$$

$$\gamma_3\gamma_4 - \gamma_5\gamma_6$$

The strain tensor in the group  $O_h$  transforms like  $\Gamma_1 + \Gamma_3 + \Gamma_5$ , and the basis functions that can be constructed are:

$$\Gamma_1 \rightarrow \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$$

$$\Gamma_3 \rightarrow \epsilon_{xx} - \epsilon_{yy}; \quad 2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}$$

$$\Gamma_5 \rightarrow \epsilon_{xy}; \quad \epsilon_{xz}; \quad \epsilon_{yz}$$

The invariant that can be constructed from these basis functions are four (the identical representation is contained four times in the direct products of the representations of the  $\gamma_i\gamma_j \otimes \epsilon$ ), and they can be obtained as:

$$\phi^{\Gamma_i} = \sum_{\lambda} \epsilon_{\lambda}^{\Gamma_i} (\gamma \otimes \gamma)_{\lambda}^{\Gamma_i}$$

where  $\lambda$  is the index of the basis functions.

## References

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- [1] T. L. Huang and A. L Ruoff, Phys. Rev. B **29**, 1112 (1984).
- [2] K. Asaumi, Phys. Rev. B **29**, 1118 (1984).
- [3] E. Knittle and R. Jaauloz, Science **223**, 53 (1984).
- [4] T. L. Huang ,K. E. Brister and A. L Ruoff, Phys. Rev. B **30**, 2968 ( 1984).
- [5] Y. K. Vohra, S. J. Duclos and A. L Ruoff, Phys. Rev. Lett. **54**, 570 ( 1985).
- [6] N. E. Christensen and S. Satpathy, Phys. Rev. Lett. **55**, 600 (1985), S. Satpathy, N. E. Christensen and O. Jepsen, Phys. Rev. B **32**,6793 (1985).
- [7] S. Baroni and P. Giannozzi, Phys. Rev. B **35**, 765 (1987).
- [8] H. K. Mao, Y. Wu, R. J. Hemley, L. C. Chen, J, F. Shu, L. W. Finger and D. E. Cox, Phys. Rev. Lett. **64**, 1749 (1990).
- [9] H. K. Mao, Y. Wu, R. J. Hemley, L. C. Chen, J, F. Shu, L. W. Finger, Science **246**, 649 (1989).
- [10] for a review see for instance W. E. Pickett, Computer Phys. Rep **9**, 115 (1989).
- [11] G. P. Kerker J. Phys. C **13**, L189 (1980).
- [12] S. Baroni, P. Giannozzi and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987 ).
- [13] P. Giannozzi, S. de Gironcoli, P. Pavone and S. Baroni, Phys. Rev. B **43**, 7231 (1991).
- [14] H. Hellmann, *Einführung in die quantumchemie*, ( Deuticke Leipzig, 1937); R. P. Feynmann *Phys. Rev.* **56**, 340 ( 1939).

- [15] O. H. Nielsen and R. M. Martin, Phys. Rev. Lett. **50**, 697 (1983).
- [16] J. H. Rose, J. R. Smith, J. Ferrante, Phys. Rev. B **28**, 1835 (1983).
- [17] F. D. Murnaghan, *Deformation of an elastic solid*, chap. 4, (John Wiley, NY, 1951).
- [18] C. Kittel, *Introduction to Solid State Physics*, ( John Wiley, NY, 1966).
- [19] for a review, see *e.g.* G. A. Samara and P. S. Peercy, Sol. State Phys., **36**, 1 (1981).
- [20] P. S. Peercy, Y. J. Fritz, Phys. Rev. Lett. **32**, 466 (1974).
- [21] see for instance, G. Y. Lyubarskii, *The application of Group Theory in Physics*, chap. 7, (Pergamon, NY, 1960).
- [22] we remind that the number of n-th order invariant for a group  $G$ , constructed from a given quantity that transform like a particular irreducible representation  $\Gamma \in G$  is the number of times the identical representation is contained in the n-th symmetric power of the representation itself.
- [23] G. F. Koster, J. O. Dimmock, R. G. Wheeler, H. Satz, *Properties of the thirty-two point groups*, ( M.I.T. Press, Cambridge, Mass., 1963).
- [24] J. C. Toledano, P. Toledano, *The Landau Theory of Phase Transitions*, (World Sci., Singapore, 1987).
- [25] J. S. Kim, D. M. Hatch, H. T. Stockes, Phys. Rev. B **33**, 1774 ( 1986).
- [26] M. V. Jarić, Phys. Rev. Lett. **48**, 1641 (1982).
- [27] D. M. Hatch, H. T. Stokes, *Isotropy Subgroups of the 230 Crystallographic Space Groups*, (World Sci., Singapore, 1988).
- [28] P. W. Anderson, E. I. Blount, Phys. Rev. Lett. **14**, 217 (1965).
- [29] W. Bührer, W. Hälg, Phys. Stat. Sol. **46**, 697 (1971).

