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LADY: SOFTWARE FOR LATTICE DYNAMICS SIMULATIONS

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INTRODUCTION

The actual rapid progress in computers stimulates the development of the mathematical models which are aimed to describe the real processes in the nature. Upgrading of such models involves, as a rule, taking account of more factors, as well as their dynamics and interaction. As a result, sometimes one obtains a model involving a great number of obscure parameters, a model within which it is already impossible to select the main factors determining the phenomenon under study.

Much the same situation is now in the field of the numerical modeling of crystal lattice dynamics. The variety of methods to calculate the electronic energy of many electron systems have been developed in quantum mechanics (or more precisely, in «quantum chemistry»). In principle, they allow us to construct the adiabatic potential surface of a crystal lattice and to calculate all the dynamical properties. However, the success of such an approach depends on a lucky choice of the quantum-chemical approximation (the basis set, the parametrization of the local density functional, etc.). Besides, the self-consistent solution of a many electron problem for a crystal with dozens of atoms in the unit cell is still beyond the potentiality of modern programs and computers. The theoretical and computing difficulty grows essentially when one tries to account the anharmonic effects and to model the thermal properties.

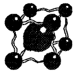
At the same time, recent publications give us some examples when it was possible, by using a simple but reasonably chosen analytical approximation of the adiabatic potential, to obtain a comprehensive description of the dynamical properties of complex crystals, including such complicate phenomena as phase transitions and polymorphism. Successfulness of these potential models is based on an appropriate combination of the quantum and classical methods. First, the electronic energy of the isolated clusters (which serve to model the analogous crystal fragments) is calculated by a non-empirical quantum-mechanical method. Then by means of numerical interpolation, the analytic interatomic potentials are drown. Finally, these potentials are used to simulate the lattice dynamics. The conceptual simplicity of this approach raises the numerical efficiency as well as facilitates the interpretation of the obtained results. Every term within such a potential model corresponds to the certain type of physical interaction, so it become possible, by revealing their relative roles, to answer not only the question «How?», but also «Why?».

Actually, there are several programs to simulate the dynamical property of crystals within a potential models (Unisoft, Climax, Molecular Simulations etc.). Each of them has the advantages and shortcomings (completeness, convenience of use, graphics etc.). We have tried to take into account disadvantages of other programs, and to develop the program package LADY (LAttice DYnamics toolkit), which allows you, having determined a potential model, to simulate different properties of a crystal, including:

- ✓ *crystal structure*
- ✓ *dynamical properties - phonon states, elastic and piezoelectric constants*
- ✓ *IR, Raman and neutron scattering spectra*
- ✓ *thermodynamic properties - temperature and pressure dependence of the crystal structure and all the above listed dynamical properties*

- ➢ *LADY incorporates many widely used potential models.*
- ➢ *LADY accomplishes an automatic account of the crystal symmetry for both the crystal structure and the phonon states.*
- ➢ *LADY is applicable for a crystal of arbitrary chemical and spatial constitution.*
- ➢ *LADY includes a graphics routines which allow you to visualize crystal structure, the calculated eigenvectors, phonon dispersion relations, DOS and many other calculated dependencies.*
- ➢ *LADY has the user-friendly interface (Win-9x, Win-2000).*

CHAPTER 1
THEORETICAL BACKGROUND



A. Zone-center lattice vibrations and elasticity

We use the following notations:
x_i - atomic coordinates (the Cartesian indexes are omitted for simplicity);
In this section only zone-center (translationally invariant) lattice deformations are considered, and hence, x_i - is the position of i-th sub-lattice in the unit cell.
u_μ - homogeneous strains which are defined by relation
$\Delta x_{i\alpha} = u_{\alpha\beta} x_{i\beta}$,
and the Voigt notations $[\alpha\beta = 11,22,33,23,13,12] \leftrightarrow [\mu = 1,2,3,4,5,6]$ are implied.

(A.1) $V(x_i, u_\mu)$ - potential function, static potential energy per unit cell;

(A.2) $V_i^x = -\dfrac{dV}{dx_i}$ - forces on atoms;

(A.3) $V_\mu^u = \dfrac{dV}{du_\mu}$ - homogeneous stresses;

(A.4) $V_{ij}^{xx} = \dfrac{d^2V}{dx_i dx_j}$ - atomic force constants;

(A.5) $V_{i\mu}^{xu} = \dfrac{d^2V}{dx_i du_\mu}$ - forces on atoms driven by the infinitesimal homogeneous strains

(A.6) $V_{\mu\nu}^{uu} = \dfrac{d^2V}{du_\mu du_\nu}$ - «external» elastic constants

(A.7) $P_i = \dfrac{dP}{dx_i}$ - effective atomic charges, where $P(x_i, u_\mu)$ - the polarization per unit cell

(A.8) $P_\mu = \dfrac{dP}{du_\mu}$ - «external» piezoelectric constants

(A.9) $\varepsilon^\infty(r_i)$ - dielectric constant

(A.10) $\varepsilon^\infty{}_i = \dfrac{d\varepsilon^\infty}{dx_i}$ - atomic derivatives of the dielectric constant

Being evaluated, the quantities (A.1 – A.10) allow us to calculate the following dynamical properties: lattice vibrations, infrared intensity, Raman scattering intensity, elastic and piezoelectric constants.

A1. Lattice vibrations

Lattice vibration calculation consists in evaluation and diagonalization of the dynamic matrix

(A1.1) $$D_{ij} = \frac{1}{\sqrt{m_i m_j}} V_{ij}^{xx} \rightarrow \sum_j D_{ij} h_{jn} = \lambda_n h_{in} .$$

Thus determined eigenvalues λ_n and eigenvectors h_{in} enable to detrmine the phonon frequencies

(A1.2) $$\omega_n = \sqrt{\lambda_n}$$

and the corresponding atomic displacements (mass-weighted eigenvectors)

(A1.3) $$e_{in} = \frac{1}{\sqrt{m_i}} h_{in} = \frac{dx_i}{dQ_n} .$$

The latter relation defines the normal coordinates Q_n which give rise to the following potential energy expressions:

(A1.4) $$V(Q) = \tfrac{1}{2} \sum_n \lambda_n Q_n^2$$

A2. Infrared intensity

is proportional to the square of the oscillator strength

(A2.1) $$\xi_n = \frac{dP}{dQ_n} ,$$

which is evaluated by means the quantities defined in Eqs.(A.7) and (A1.3) as

(A2.2) $$\xi_n = \sum_i P_i e_{in} .$$

The corresponding contribution of the mode n to the static dielectric constant is

(A2.3) $$\Delta\varepsilon_n = \frac{4\pi}{\lambda_n v_c} \xi_n^2 ,$$ where v_c is the unit cell volume.

Other important characteristics of the IR spectrum are longitudinal (LO) frequencies, which are determined from the transversal (TO) frequencies (A1.2) and the dielectric strengths (A2.3) as the roots of the dielectric function

(A2.4) $$\varepsilon(\omega) = \varepsilon^\infty + \frac{4\pi}{v_c} \sum_n \frac{\xi_n^2}{\omega_n^2 - \omega^2}$$

A3. Raman scattering intensity

Raman scattering intensity is proportional to the square of the derivative

(A3.1) $$\zeta_n = \frac{d\varepsilon^\infty}{dQ_n} ,$$

which is evaluated by means the quantities defined in Eqs. (A.8) and (A1.3) as

(A3.2) $$\zeta_n = \sum_i \varepsilon_i^\infty e_{in} .$$

A4. Elastic constants

The elastic constant expression includes «external» term (A.6) and the atomic relaxation contribution. The latter can be easily written by introducing the magnitude of the atomic relaxation along the normal coordinate Q_n under homogeneous strain u_μ

(A4.1) $$Q_{n\mu} = \frac{dQ_n}{du_\mu} = -\frac{1}{\lambda_n} V_{n\mu},$$

where

(A4.2) $$V_{n\mu} = \frac{d^2V}{dQ_n du_\mu} = \sum_i V^{xu}_{i\mu} e_{in}.$$

Then the total elastic constant expression can be written as

(A4.3) $$C_{\mu\nu} = \frac{1}{v_c}\left(V^{uu}_{\mu\nu} - \sum_n \lambda_n Q_{n\mu} Q_{n\nu} \right).$$

A5. Piezoelectric constants

The piezoelectric constant expression also includes «external» term (A.7) and the atomic relaxation contribution. The latter can be easily determined through the quantities defined in Eqs. (A2.2) and (A4.1). The total piezoelectric constants can be expressed as

(A5.1) $$E_\mu = \frac{1}{v_c}\left(P_\mu - \sum_n \xi_n Q_{n\mu} \right)$$

A6. Symmetry analysis

Symmetry analysis of the vibrational states consists in using the symmetry coordinates – the linear combinations of the atomic displacements - which have a specific transformation character with respect to the symmetry operations S_g, i. e. which belong to different irreducible representations of the crystal symmetry group. Such combinations can be written through the character of the irreducible representation χ^R_g as follows:

(A6.1) $$s^R_i = \sum_g \chi^R_g S_g(x_i)$$

After orthogonalization of all the possible s^R_i belonging to the same considered irreducible representation *R*, one obtains the basis of this representation. Being transformed to this basis, the dynamic matrix get a quasi-diagonal block form, and every block corresponds to different irreducible representation.

A7. Frequency differentiation

Frequency differentiation with respect to the potential model parameters serves for two purposes. First of all this is an effective tool to adjust the parameters in order to concord the calculated and observed spectra. Secondly, this helps to elucidate the microscopic origin of the vibrational states. Let us consider an arbitrary parameter *p* of the potential function. The dynamic matrix (A1.1), its eigevalues (A1.2) and eigenvectors (A1.3) would depend on *p*. From Eq. (A1.1 - A1.3) one can derive the following relation between these quantities:

(A7.1) $$\lambda_n(p) = \sum_{ij} e_{in}(p) V_{ij}(p) e_{jn}(p).$$

In order to calculate the first derivatives of the eigenvalues λ_n with respect to *p*, one can neglect the *p*-dependence of the eigenvectors. So, the following relation is valid:

(A7.2) $$\frac{d\lambda_n}{dp}=\sum_{ij} e_{in}\frac{dV_{ij}}{dp}e_{jn}.$$

Thus, only implicit p-dependence of the adopted potential function should be taken into account in Eq.(A7.2). The peculiarity of this procedure within all the possible potential functions are discussed in Sec. D.

A8. Elastic constant differentiation

Elastic constant differentiation with respect to the potential model parameters is not so easy task because of complexity of Eq. (A4.3) No simplifying relation, analogous to (A7.2), is valid in this case. However, we can offer an approximation, which was found to be quite accurate. Usually, the model potential function is expressed in terms of variation of any internal coordinates q_n - inter-atomic distances or valence angles. Then, the elastic constants an be written as

(A8.1) $$C_{\mu\nu}=\frac{1}{v_c}\left(\sum_{m<n}\frac{dq_m}{du_\mu}V^{qq}_{mn}\frac{dq_n}{du_\mu}+\sum_n V^q_n\frac{d^2q_n}{du_\mu du_\nu}\right),$$

where the derivatives

(A8.2) $$V^{qq}_{mn}=\frac{d^2V}{dq_m dq_n}\text{ and }V^q_n=\frac{dV}{dq_n}$$

can be explicitly expressed in frame of a particular potential model. It is also implied that the dependence q_n on u_μ includes the atomic relaxation contribution described in Eq. (A4.1):

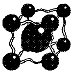
(A8.3) $$\frac{dq_n}{du_\mu}=\frac{\partial q_n}{\partial u_\mu}+\sum\frac{\partial q_n}{\partial x_i}X_{i\mu},$$

where

(A8.4) $$X_{i\mu}=\sum_n e_{in}Q_{n\mu}$$

Numerical calculations show that the second term in Eq. (A8.1) is of minor importance with respect to the first one. Hence a good approximation for the derivative of the elastic constant with respect to potential model parameter p is following:

(A8.5) $$\frac{dC_{\mu\nu}}{dp}\approx\frac{1}{v_c}\left(\sum_{m<n}\frac{dq_m}{du_\mu}\frac{dV^{qq}_{mn}}{dp}\frac{dq_n}{du_\mu}\right)$$



B. Phonon states

B1. Phonon dispersion

The phonon dispersion study consists in analysis of the phonon frequencies variation along some chosen directions in the Brillouin zone (BZ).

When considering the finite wave-vector lattice vibrations one should consider the individual atomic displacements. Hence, index *i* in the above sub-lattice coordinates x_i must be replaced by a combination (i,I_a,I_b,I_c), where *i* is as previously the number of a sub-lattice and the 3D index $I=(I_a,I_b,I_c)$ numerates the cells in the lattice, i.e. shows the number of translations along *a, b* and *c*-axes correspondingly.

At finite wave-vector *k* the dynamic matrix is defined as

(B1.1) $$D_{ij}(k)=\frac{1}{\sqrt{m_i m_j}}\sum_J V^{xx}_{iI,jJ}\exp[ik(x_{jJ}-x_{iI})]$$

Diagonalisation of this complex (self-conjugated) matrix gives the phonon frequencies $\omega_n(k)$ and phonon eigenvectors $e_{in}(k)$, and the relations analogous to (A1.1 - A1.4) are valid.

The same symmetry analysis procedure (A6.1) is applicable in the phonon dispersion study,. But now the symmetry subgroup corresponding to the chosen wave-vector direction must be considered. This subgroup includes only those symmetry operations which keep *k*-vector invariant. The phonon dispersion symmetry analysis provides a powerful tool to solve the problem of the phonon branches crossing.

B2. Brillouin-zone scanning

Brillouin-zone scanning is necessary to obtain the information about the whole phonon spectrum. Such a scanning consists in $D(k)$-matrix diagonalization over the 3D-net of wave-vector $k=\left(\frac{a^*}{n_1},\frac{b^*}{n_2},\frac{c^*}{n_3}\right)$, at $n_1,n_2,n_3=-N,\dots,N$. In total, this includes $N_t=(2N+1)^3$ points in BZ. The volume of calculations is drastically diminished by taking into account the symmetry relations in *k*-space:

(B2.1) $$\omega_n(S_g(k))=\omega_n(k)$$
$$e_{in}(S_g(k))=S_g(e_{in}(k))$$

B3. Density-of-state

Density-of state (DOS) function is determined by summation over all the phonon states:

(B3.1) $$g(\omega)=\frac{1}{N_t}\sum_{n,k}\delta(\omega-\omega_n(k))$$

B4. Partial atomic density-of-state

Partial atomic density-of-state shows the contribution of different atoms to DOS. They are defined as

(B4.1) $$g_i(\omega) = \frac{1}{N_t}\sum_{n,k}\delta(\omega - \omega_n(k))\frac{|e_{in}(k)|^2}{\sum_j |e_{jn}(k)|^2}.$$

B5. Thermodynamic functions

Thermodynamic functions (more exactly, the corresponding phonon contribution) are calculated within harmonic approximation as follows:

(B5.1) Free energy: $$F^p(T) = \frac{k_B T}{N_t}\sum_{n,k}\ln(2\sinh(\beta_{nk}))$$

(B5.2) Entropy: $$S(T) = \frac{1}{N_t}\sum_{n,k}[\beta_{nk}\coth(\beta_{nk}) - \ln(2\sinh(\beta_{nk}))]$$

(B5.3) Heat capacity: $$C(T) = \frac{1}{N_t}\sum_{n,k}\left[\frac{\beta_{nk}}{2\sinh(\beta_{nk})}\right]^2$$

where $\beta_{nk} = \dfrac{h\omega_n(k)}{2k_B T}$

B6. Atomic thermal parameters (ATP)

Atomic thermal parameters (ATP), or atomic thermal amplitudes, are determined by the expression:

(B6.1) $$a_{i,\alpha\beta}(T) = \frac{1}{N_t}\sum_{nk}\frac{h}{2\omega_n(k)}\coth(\beta_{nk})e_{i\alpha}(k)e_{i\beta}(k)$$

B7. Pair distribution function (PDF)

Pair distribution function (PDF) - the probability distribution of the interatomic distances - within the quasiharmonic approximation is determined by the expression:

(B7.1) $$f(R,T) = \sum_n \frac{1}{\sqrt{\pi\sigma_n}}\exp\left(-\frac{(R-R_n)^2}{\sigma_n}\right)$$

Here R_n is the temperature-dependent distance between atoms i and j which is related to the static equilibrium interatomic distance R_{n0} by the relation:

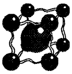
$$R_n^2(T) = R_{n0}^2 + \sigma_n$$

And σ_n is the corresponding dispersion determined by the relation:

$$\sigma_n = \langle u_i u_i\rangle + \langle u_j u_j\rangle - 2\langle u_i u_j\rangle$$

The isotropic atomic displacement correlation is defined by the relation similar to (B6.1):

(B7.2) $$\langle u_i u_j\rangle = \frac{1}{N_t}\sum_{nk}\frac{h}{2\omega_n(k)}\coth(\beta_{nk})(e_{ix}e_{jx} + e_{iy}e_{jy} + e_{iz}e_{jz}).$$



C. Geometry optimization

The self-consistent harmonic approximation demands that all second energy derivatives (A.4-A.6), which determine the dynamical properties, should be taken at the static equilibrium lattice configuration. It means that the first derivatives (A.2-A.3) must be equal to zero. This is the Static Equilibrium Condition (SEC):

$$\begin{aligned} &V_i^x = 0 \\ &V_\mu^u = 0 \end{aligned} \qquad \text{(C.1)}$$

Generally, there are two manners to deal with SEC. The fist one is to use the experimental geometry and to impose the conditions (C.1) thus adjusting the potential model parameters. The second approach is non-empirical. It involves the solution of the Eq.(C.1) within the adopted potential model. In such a case, the agreement between calculated and experimental geometries serves as an important criterion of validity of the model.

The computational solution of Eq.(C.1) consists in step-by-step variation of the geometry parameters (atomic positions and the unit cell dimensions and angles), thus diminishing the potential energy. The steepest descent method provides us a simple and effective way to solve this task. It seems to be quite suitable because we have possibility to calculate the second derivatives (A.4-A.6) Two types of the geometry parameters – the atomic positions and the unit cell dimensions – have rather different scale of variation. The unit cell parameters can be easily optimized by means of relation:

$$\Delta u_\mu = -\sum_\nu (v_c C_{\mu\nu})^{-1} V_\nu^u \, . \qquad \text{(C.2)}$$

So, by using this relation one can find the optimal cell parameters in few steps. The atomic position optimization is a more difficult task because of great number of degrees of freedom and the strong coupling between them. In principle, the same steepest descent relation

$$\Delta x_i = -\sum_j V_{ij}^{-1} V_j^x \qquad \text{(C.3)}$$

can be used. The last expression describes the transformation in space of 3N Cartesian displacements. To diminish the symmetry breaking due to the finite numerical accuracy, it is highly advisable to transform this relation in space of the normal coordinates. The relation (C.3) in the normal coordinate space is very simple:

$$\Delta Q_n = -\frac{1}{\lambda_n} V_n \, , \qquad \text{(C.4)}$$

where

$$V_n = \sum_i V_i^x e_{in} \qquad \text{(C.5)}$$

is the force conjugated to normal coordinate Q_n. The most advantage is that only the totally symmetric coordinates (belonging to the symmetry representation A1 or Ag) should be taken into consideration in (C.4). This conserves the lattice symmetry and diminishes the volume of calculation.

C1. Pressure-induced geometry variation

The static equilibrium conditions (C.1) are valid for a crystal at zero temperature and in absence of the external pressure. In order to simulate the crystal structure at non-zero external pressure p these conditions must be changed as follows:

$$V_i^x = 0$$

(C1.1) $$V_{xx}^u = V_{yy}^u = V_{zz}^u = -pv_c$$

$$V_{yz}^u = V_{xz}^u = V_{xy}^u = 0$$

The same geometry optimization procedure enables us to solve the Eq.(C1.1). The only change is to replace in Eq.(C.3) V_ν^u by $V_\nu^u + pv_c$ for $\nu = xx, yy, zz$. The concomitant calculation of the phonon states, the elastic and piezoelectric properties provides us a tool to study the influence of external pressure on the dynamical properties of the crystal under study.

C2. Finite-temperature simulation

On studying the crystal structure at finite temperature, one should minimize not the static potential energy but the free energy. Often, for this purpose one uses the quasiharmonic approximation (QHA) which consists in applying the phonon representation (A1.4), i.e. the second order decomposition of the potential function around the thermodynamically average lattice configuration $\bar{x}$. In this case the phonon frequencies become geometry dependent:

(C2.1) $$V(\bar{x},Q) = V(\bar{x}) + \tfrac{1}{2}\sum_n \lambda_n(\bar{x})Q_n^2 .$$

Here for simplicity the summation over *n* implies the summation over all the phonon branches and over all the wave vectors in BZ as well. Within QHA, the free energy is the sum of potential energy and the phonon contribution (B5.2):

(C2.2) $$F(\bar{x},T) = V(\bar{x}) + F^p(\lambda_n(\bar{x}),T).$$

It is important to emphasize that the phonon frequencies are geometry dependent in QHA. Then the condition of the thermodynamic equilibrium is as follows:

(C2.3) $$\frac{dF}{d\bar{x}_i} = -V_i(\bar{x}) + \sum_n \frac{dF^p(\lambda_n,T)}{d\lambda_n}\frac{d\lambda_n(\bar{x})}{d\bar{x}_i} = 0 .$$

The last term in this expression can be considered as the temperature-induced phonon force V_i^p:

(C2.4) $$V_i(\bar{x}) = V_i^p(\bar{x},T).$$

By replacing $\bar{x}_i$ in (C2.3 - C2.4) by $\bar{u}_\mu$ we obtain the equation for the temperature-induced homogeneous strains, which determine the thermal expansion. Thus, by solving the equation (C2.3 - C2.4) at a gradually increased *T* value one obtains the dependencies $\bar{x}(T)$ and $\bar{u}_\mu(T)$ which completely describe the temperature-induced structure evolution. The derivatives of the phonon frequencies with respect to the geometry parameters (the so called Gruneisen constants) can be easily calculated by means of the expression analogous to (A7.2).

In the same way as in the static energy optimization (C.4), it is recommended to replace the individual atomic coordinates by the normal zone-center coordinates Q_n. This reduces the volume of calculations and ensures the symmetry conservation. As concerns to differentiation with respect to homogeneous strains, it should be noted that at finite wave *k* one must deal with not an individual mode but with the sum over the star $S_g(k)$. Thus the corresponding derivative in Eq.(C2.3) must be taken as: $\sum_g \frac{d\lambda_n(S_g(k))}{du_{\alpha\beta}} = \sum_g S_{\alpha\gamma}^g \frac{d\lambda_n}{du_{\gamma\delta}} S_{\beta\delta}^g$

The concomitant calculation of the phonon states, the elastic and piezoelectric properties provides us a tool to study the influence of temperature on the dynamical properties of the crystal under study.

D. Potential models

LADY calculates all the quantities (A.1-A.11) within the adopted potential model whenever it is possible. The following restrictions are inherent to different models:

Model	Undefined quantities
VFF	1 –3
IAP	7 – 10
RIM	9 – 10
PIM	-
SM	-

D1. Valence force field (VFF)

This model is based on considering the variation of the valence coordinates q_n, which include the bond stretching s_n and the valence angle bending b_n. PF is considered as a quadratic form in the space of the valence coordinate increments:

(D1.1) $$V(q) = \tfrac{1}{2}\sum_{mn} F_{mn}\Delta q_m \Delta q_n$$

The coefficients F_{mn} are valence force constants. All the calculation within VFF involve B^x-matrix - the first derivatives of q_n with respect to atomic displacements:

(D1.2) $$B^x_{ni} = \frac{dq_n}{dx_i}$$

and the B^u-matrix - the first derivatives of q_n with respect to homogeneous strains:

(D1.3) $$B^u_{n\mu} = \frac{dq_n}{du_\mu}$$

Then the second derivatives (D1.4-D1.6) are expressed as following:

(D1.4) $$V_{ij} = F_{mn}B^x_{mi}B^x_{nj}$$

(D1.5) $$V_{i\mu} = F_{mn}B^x_{mi}B^u_{n\mu}$$

(D1.6) $$V_{\mu\nu} = F_{mn}B^u_{m\mu}B^u_{n\nu},$$

here and further the summation over the repeated indexes is implied.

To calculate the IR and Raman intensities, VFF model is supplied by valence bond polarization scheme. This involves representation of crystal polarization and polarizability as an additive sum of contributions of valence bonds:

(D1.7) $$\mathbf{P} = \sum_n \mathbf{p}_n$$

(D1.8) $$\varepsilon^\infty = \sum_n \varepsilon_n$$

In addition, it is supposed that

- the valence bond dipole moment p_n is directed along the bond, and its magnitude depends on bond length;
- the valence bond polarizability ε_n has two independent component ε^1_n and ε^2_n,

correspondingly parallel and perpendicular to the bond direction, and their magnitude also depend on the bond length.

Thus, every valence bond s_n is characterized, besides force constant

(D1.9) $$F_{nn} = \frac{d^2V}{ds_n^2},$$

by three polarization parameters:

(D1.10) $$Z_n = \frac{dp_n}{ds_n}, \quad E_n^1 = \frac{d\varepsilon_n^1}{ds_n} \text{ and } E_n^2 = \frac{d\varepsilon_n^2}{ds_n}.$$

The valence angle b_n is built of two atom-shared valence bonds s_n^1 and s_n^2. General VFF model (D1.1) takes into account not only diagonal force constants (like (D1.9)) but non-diagonal ones (with $n \neq m$) as well. Within LADY it is possible to deal with s_n^1 - s_n^2, b_n - s_n^1 and b_n - s_n^2 cross-terms.

Thus, every valence angle b_n is characterized, besides diagonal force constant

(D1.11) $$F_{nn} = \frac{d^2V}{db_n^2},$$

by three non-diagonal force constants:

(D1.12) $$H_n = \frac{d^2V}{ds_n^1 ds_n^2}, \quad A_n^1 = \frac{d^2V}{db_n ds_n^1} \text{ and } A_n^2 = \frac{d^2V}{db_n ds_n^2}.$$

The set of VFF parameters (D1.9-D1.12) enables us to calculate the phonon states, IR and Raman scattering intensities, elastic and piezoelectric constants.

Usually one considers VFF model as an essentially harmonic approximation, i.e. only linear relation (D1.2-D1.3) between valence coordinates and atomic displacements are taken into account. At such approach, the given crystal geometry is considered to correspond to static equilibrium, and nor geometry optimization neither temperature or pressure dependence could be studied within this model. However, one can overcome this shortcoming by extrapolating Eq. (D1.1) to the finite valence coordinate variation. In addition, it is possible to incorporate the «proper» anharmonicity by supposing the valence force constants to be coordinate-depended. Then one obtain the following potential function:

(D1.13) $$V(q(x)) = \tfrac{1}{2}\sum_{mn} F_{mn}(q)(q_m - q_m^0)(q_n - q_n^0),$$

where the true $q(x)$ dependence is implied. In order to calculate the second derivatives (D1.4-D1.6) with potential function (D1.13), one needs the second-order B-matrixes

(D1.14) $$B_{nij}^{xx} = \frac{d^2q_n}{dx_i dx_j}$$

(D1.15) $$B_{ni\mu}^{xu} = \frac{d^2q_n}{dx_i du_\mu}$$

(D1.16) $$B_{n\mu\nu}^{uu} = \frac{d^2q_n}{du_\mu du_\nu}.$$

D2. Inter-atomic potentials (IAP)

Within this model only pair-wise interactions are considered. They are described by any analytical function $\phi(R_{ij})$ of inter-atomic distance $R_{ij} = |x_j - x_i|$. The corresponding potential function is expressed as

$$V = \sum_{i<j} \phi(R_{ij})$$

Let us define vector $r = x_j - x_i$ (atomic indexes *i* and *j* are omitted for simplisity). Then the corresponding contributions to all the quantities (A.2-A.6) can be easily expressed through two parameters $A = \phi''$ and $B = \phi'/R$ (so called longitudinal and transversal force constants) as follows:

(A2) $$V_{i\alpha} = Br_\alpha$$

(A3) $$V_{\alpha\beta} = Br_\alpha r_\beta$$

(A4) $$V_{i\alpha,j\beta} = (A-B)\frac{r_i r_\beta}{r^2} + \delta_{\alpha\beta}B$$

(A5) $$V_{i\alpha,\beta\gamma} = (A-B)\frac{r_\alpha r_\beta r_\gamma}{r^2} + \tfrac{1}{2}B(\delta_{\alpha\beta}r_\gamma + \delta_{\alpha\gamma}r_\beta)$$

(A6) $$V_{\alpha\beta,\lambda\mu} = \left((A-B)\frac{r_\alpha r_\lambda}{r^2} + \delta_{\alpha\lambda}B\right)r_\beta r_\mu$$

Within LADY 1 aJ = 10^{-18}J is assumed as the energy unit and 1 Å for all the spatial dimensions. Several standard analytic expressions for $\phi(r)$ are available. All of them involve two parameters *a* and *b*. These standard functions as well as the corresponding parameter units are listed in following table:

Type of function	***Key***	$\phi(r)$	***a unit***	***b unit***
Born-Karman model	BKM	$a = \phi''\quad b = \phi'/r$	aJ/Å^2	aJ/Å^2
Harmonic function	HAR	$\frac{1}{2}a(r-b)^2$	aJ	Å
Exponent function	EXP	$a\exp\left(-\frac{r}{b}\right)$	aJ	Å
Power function	POW	ar^{-b}	aJ/Å^b	-
Coulomb low	COU	$\frac{ab}{r}$	*e*	*e*

D3. Rigid ion model (RIM)

Within RIM a crystal is considered to consist of isolated spheric ions with ionic charges z_i, and the potential function is presented as a sum of non-Coulomb and electrostatic contributions:

(D3.1) $$V^{RIM}(x) = U(x) + \frac{1}{2}\sum_{i,j}\frac{z_i z_j}{r_{ij}}.$$

Non-Coulomb contribution is usually treated by the above considered IAP potentials. The electrostatic interaction gives the following contributions in the first and second energy derivatives:

(D3.2) $$V_i = U_i - z_i e_i \text{, where } e_{i\alpha} = \sum_j \frac{z_j r_{ij\alpha}}{r_{ij}^3}$$

(D3.3) $$V_{ij} = U_{ij} - z_i C_{ij} z_j \text{, where } C_{i\alpha j\beta} = \frac{z_i z_j}{r_{ij}^3}\left(3\frac{r_{ij\alpha} r_{ij\beta}}{r_{ij}^2} - \delta_{\alpha\beta}\right)$$

The convergence of the Coulomb sum in (D3.1-D3.3) is very slow and conventional, i.e. the result depends on the choice of partial sums. Physically, it means that the electrostatic field in dielectrics depends on the shape of the sample. Usually, one can neglect this effect, and so, one needs to eliminate this conventionally converged contribution. It is easily done by means of Ewald transformation. Below, the final expressions of this method are presented.

Let us consider at site **r** the Coulomb potential which is due to a simple crystal lattice of the unit charges $\varphi(\mathbf{r}) = \sum_{\mathbf{I}} \frac{1}{|\mathbf{I}+\mathbf{r}|}$, here $\mathbf{I} = (i_1 a, i_2 b, i_3 c)$ is the 3D lattice vector. Within the Ewald method, this sum is transformed into two absolutely and quickly converged sums over the direct (**I**) and reciprocal (**K**) lattices: $\varphi(\mathbf{r}) = \sum_{\mathbf{I}} H(|\mathbf{I}+\mathbf{r}|, g) + \frac{4\pi}{v}\sum_{\mathbf{K}} \cos(\mathbf{Kr}) G(K, g)$, where $H(x,g) = \frac{erfc(gx)}{x}$ and $G(x,g) = \frac{1}{x^2}\exp\left(-\frac{x^2}{4g^2}\right)$.

The optimal value of the splitting constant g is taken as $g = \frac{\sqrt{\pi}}{v^{\frac{1}{3}}}$. Let us denote $\mathbf{R} = \mathbf{I} + \mathbf{r}$.

Then the first and the second derivatives with respect to r_α and $u_{\mu\nu}$ can be expressed as follows:

$$\varphi'_\alpha = \sum_{\mathbf{I}} H' \frac{R_\alpha}{R} - \frac{4\pi}{v}\sum_{\mathbf{K}} \sin(\mathbf{Kr}) G(K,g) K_\alpha$$

$$\varphi'_{\mu\nu} = \sum_{\mathbf{I}} H' \frac{R_\mu R_\nu}{R} - \frac{4\pi}{v}\sum_{\mathbf{K}} \cos(\mathbf{Kr})\left[G\delta_{\mu\nu} + G'\frac{K_\mu K_\nu}{K}\right]$$

$$\varphi''_{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{I}} \exp(i\mathbf{qR})\left[\frac{H'}{R}\delta_{\alpha\beta} + \left(H'' - \frac{H'}{R}\right)\frac{R_\alpha R_\beta}{R^2}\right] +$$

$$+\frac{4\pi}{v}\sum_{\mathbf{K}} \exp\left(i(\mathbf{K}+\mathbf{q})\mathbf{R}\right)(K+q)_\alpha (K+q)_\beta G(K+q, g)$$

$$\varphi''_{\alpha,\mu\nu} = \sum_{\mathbf{I}}\left[H'\frac{\delta_{\alpha\mu}R_\nu + \delta_{\alpha\nu}R_\nu}{2R} + \left(H'' - \frac{H'}{R}\right)\frac{R_\alpha R_\mu R_\nu}{R^2}\right] +$$

$$+\frac{4\pi}{v}\sum_{\mathbf{K}} \cos(\mathbf{Kr})\left[G(\delta_{a\nu}K_\mu + \delta_{a\mu}K_\nu) + G'\frac{K_\alpha K_\mu K_\nu}{K}\right]$$

$$\varphi''_{\alpha\beta,\mu\nu} = \sum_{\mathbf{I}}\left[\delta_{\alpha\mu}H'\frac{R_\mu R_\nu}{R} + \left(H'' - \frac{H'}{R}\right)\frac{R_\alpha R_\beta R_\mu R_\nu}{R^2}\right] + \frac{4\pi}{v}\sum_{\mathbf{K}} \cos(\mathbf{Kr})\Big[G\left(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}\right) +$$

$$+\left(G'' - \frac{G'}{K}\right)\frac{K_\alpha K_\beta K_\mu K_\nu}{K} + \frac{G'}{K}(\delta_{\alpha\mu}K_\beta K_\nu + \delta_{\beta\mu}K_\alpha K_\nu + \delta_{\alpha\nu}K_\beta K_\mu + \delta_{\beta\nu}K_\alpha K_\mu + \delta_{\mu\nu}K_\alpha K_\beta)\Big]$$

D4. Polarizable ion model (PIM)

Polarizable Ion Model (PIM) is an extension of RIM, which takes into account the proper ionic polarizability α_i. Within this model all ions in the crystals possess a proper dipole moment $p_i = \alpha_i e_i$, where e_i is the electric field strength. The corresponding extension of the potential function is as follows:

$$V^{PIM}(x,p) = V^{RIM}(x) + \frac{1}{2}\sum_{i,j} S_{ij}(x) p_i p_j - \sum_{i} p_i e_i(x)$$

$$S_{ij} = \frac{\partial^2 V}{\partial p_i \partial p_j} = \frac{1}{\alpha_i}\delta_{ij} - C_{ij}(x)$$

$$V_p = \left.\frac{\partial V}{\partial p_i}\right|_{p=0} = e_i$$

$$V_{px} = \frac{\partial^2 V}{\partial p_i \partial x_j} = -C_{ij} z_j - \delta_{ij} d_i^0 \text{, where } d_i^0 = \sum_j C_{ij} z_j$$

Then the following relations are valid:

$$\frac{dV}{dp} = 0 \Rightarrow p^0 = S^{-1} V_p$$ - static polirization

$$V(x,p) = V^{RIM}(x) - \frac{1}{2} p^0 V_p$$ - static energy

$$\varepsilon^{\infty} = 1 + \frac{4\pi}{v_c}\sum_{ij}\left(S^{-1}\right)_{ij}$$ - dielectric constant

$$\frac{dp}{dx} = -S^{-1} V_{px}$$ - dynamic polarization

$$\frac{d^2 V}{dx^2} = V_{xx} - \frac{1}{2} V_{xp} S^{-1} V_{px}$$ - force constants

$$\tilde{z}_i = z_i + \sum_j \frac{dp_j}{dx_i}$$ - effective charges

D5. Shell model (SM)

Shell model (SM) is an extension of RIM, which takes into account the proper ionic polarization induced by the electric field and by the short-range interactions as well. Within this model all ions in the crystals possess proper dipole moment:

$$p_i = \alpha_i e_i + \kappa_i U_i,$$

where e_i is the electric field strength and U_i is the force caused by the short-range interactions. An additional parameter κ_i is incorporated within SM in comparison with PIM. This representation of SM model differs from the more common description of SM, which considers the ionic polarization as displacements of the massless ionic shells with the charges y_i. In fact, the relation

$$\kappa_i = \frac{\alpha_i}{y_i}$$

is valid, and both the definitions are equivalent. Below we shall use the 'traditional' parameters y_i. The corresponding extension of the potential function is as follows:

$$V^{SM}(x,p) = U(x_i + \frac{p_i}{y_i}) + \frac{1}{2}\sum_{i,j}\frac{z_i z_j}{r_{ij}} + \frac{1}{2}\sum_{i,j} S_{ij}(x) p_i p_j - \sum_i p_i e_i(x)$$

$$S_{ij} = -C_{ij}(x) + \frac{U_{ij}}{y_i y_j} + \delta_{ij}\left(\frac{1}{\alpha_i} - \frac{d_i^0}{y_i} + \frac{u_i^0}{y_i^2}\right), \text{ where } u_i^0 = \sum_j U_{ij}$$

$$V_p = e_i - \frac{U_i}{y_i}$$

$$V_{px} = \frac{\partial^2 V}{\partial p_i \partial x_j} = -C_{ij} z_j + \frac{U_{ij}}{y_i y_j} + \delta_{ij}\left(\frac{u_i^0}{y_i} - d_i^0\right)$$

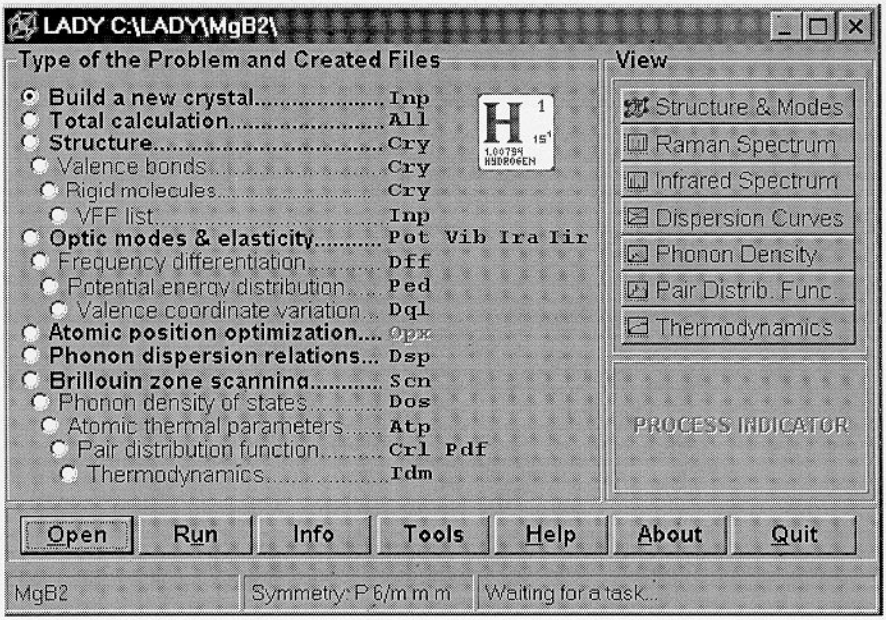
CHAPTER 2
SCHEME OF ORGANIZATION. ROUTINES AND FILES

The package LADY consists of several computational routines which serve to solve different tasks. There are 5 principal routines:

- *Structure*
- *Optic modes & elasticity*
- *Geometry optimization*
- *Phonon dispersion relations*
- *Brillouin zone scanning*

and several auxiliary routines (Fig. 1):

- *Valence bonds*
- *VFF list*
- *Rigid Molecules*
- *Frequency differentiation*
- *Potential energy distribution*
- *Valence coordinate variation*
- *Phonon density-of-state*
- *Atomic thermal parameters*
- *Pair distribution function*
- *Thermodynamics*



LADY C:\LADY\MgB2\

Type of the Problem and Created Files

- ● **Build a new crystal**.................... Inp
- ○ **Total calculation**........................ All
- ○ **Structure**.................................... Cry
  - ○ Valence bonds............................ Cry
    - ○ Rigid molecules.......................... Cry
      - ○ VFF list.. Inp
- ○ **Optic modes & elasticity**.......... Pot Vib Ira Iir
  - ○ Frequency differentiation........... Dff
    - ○ Potential energy distribution...... Ped
      - ○ Valence coordinate variation... Dql
- ○ **Atomic position optimization**.... Opx
- ○ **Phonon dispersion relations**... Dsp
- ○ **Brillouin zone scanning**........... Scn
  - ○ Phonon density of states........... Dos
    - ○ Atomic thermal parameters...... Atp
      - ○ Pair distribution function.......... Crl Pdf
        - ○ Thermodynamics....................... Tdm

MgB2 | Symmetry: P 6/m m m | Waiting for a task...

Figure 1. LADY program shell

The input-output data exchange between all the routines is accomplished by means of several files. All these files have the same extension *.ldy* but different names:

inp.ldy	input data
cry.ldy	output for *Structure*, *Valence bonds* and *Rigid Molecules*

output for *Optic modes & elasticity*:

pot.ldy	potential energy and its first and second derivatives
vib.ldy	zone-center vibrations, elastic and piezoelectric constants
iir.ldy	infrared spectrum simulation
ira.ldy	Raman spectrum simulation

dff.ldy	output for *Frequency differentiation*
ped.ldy	output for *Potential energy distribution*
dql.ldy	output for *Valence coordinate variation*
opx.ldy	output for *Geometry optimization*
dsp.ldy	output for *Phonon dispersion relations*
scn.ldy	output for *Brillouin zone scanning*
dos.ldy	output for *Phonon density-of-state*
atp.ldy	output for *Atomic thermal parameters*
pdf.ldy	output for *Pair distribution function*
tdm.ldy	output for *Thermodynamics*

The package also includes some standard data (space symmetry groups, atomic parameters, the table of irreducible representations and the list of subgroups) which are stored in *lady.dat* file. The auxiliary *inf.ldy* file is opened automatically, and some brief information about LADY running is written there. You can look there for diagnostics in case of some errors.

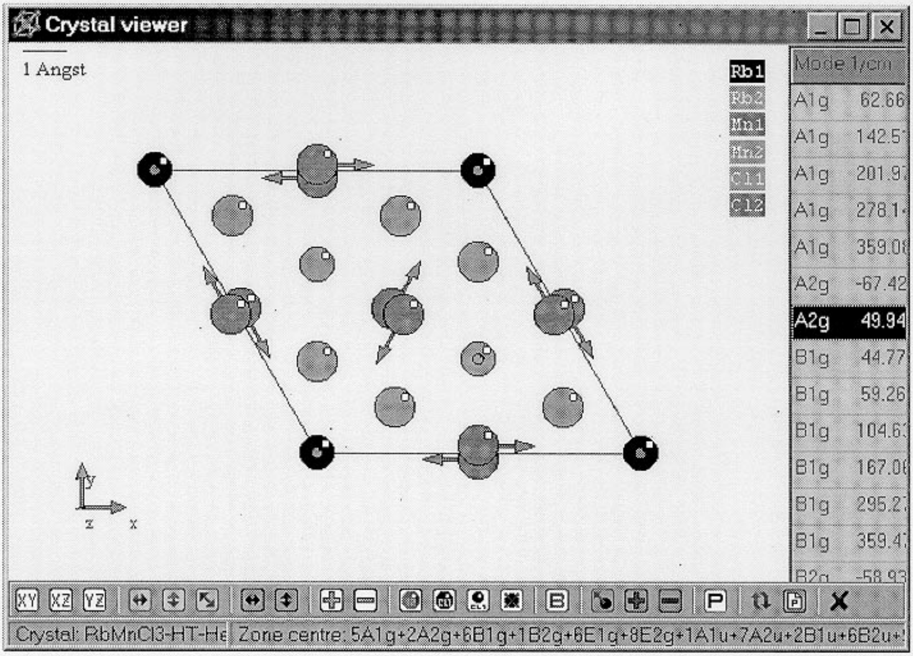
Structure

This routine uses the input data from the STRUCTURE section of *inp.ldy* file (*Space symmetry group*, *elementary unit cell* parameters and *atomic composition*) and generates an extended description of the crystal structure (the table of symmetry transformations, the *atomic coordinates* and the *interatomic distances*). When running, this program applies to *lady.dat* file, which contains all the space symmetry groups and the list of standard atomic parameters.

The results are written in *cry.ldy* file, and the generated crystal structure can be visualized by *Structure & Modes* viewer (Fig 2).

Valence bonds

This is an auxiliary routine which can follow the *Structure* routine. It provides us the useful information about the coordination polyhedra around the atoms. Before initiating this routine you should mark some *interatomic distances* (namely those which you consider as valence bonds) in *cry.ldy* by asterisk in first position. This routine builds the valence environment for



Mode	1/cm
A1g	62.66
A1g	142.5
A1g	201.9
A1g	278.1
A1g	359.0
A2g	-67.42
A2g	49.94
B1g	44.77
B1g	59.26
B1g	104.6
B1g	167.0
B1g	295.2
B1g	359.4
B2g	-58.93

Crystal: RbMnCl3-HT-He

Zone centre: 5A1g+2A2g+6B1g+1B2g+6E1g+8E2g+1A1u+7A2u+2B1u+6B2u+

Figure 2. Structure & Modes viewer

all the atoms, i.e. the number and orientation of the valence bonds and gives the list of valence angles. This information is written in the end of *cry.ldy* file.

VFF list

This is an auxiliary routine which can follow the *Valence bonds* routine. It is very useful if you wish to use the VFF contribution. This routine creates the complete list of valence coordinates in the POTENTIAL section of *inn.ldy* file. Afterwards you can choose the necessary valence coordinates and to assign the force constants values. All other valence coordinates could be omitted for simplicity.

Optic modes & elasticity

This command initiates consequent execution of several routines.

The first one elaborates the input data from POTENTIAL section in *inp.ldy* file and calculates the lattice energy and all its first and second derivatives with respect to atomic displacements and homogeneous strains: forces on atoms, external tensions, atomic force constants, polarization and polarizability derivatives. All these data are written in *pot.ldy* file.

The second routine performs the zone-center vibrational states calculation. It calculates frequencies, eigenvectors, polarization and polarizability derivatives and gives the symmetry assignment for all the zone-center modes.

These results are written in *vib.ldy* file, and the calculated eigenvectors can be visualized by *Structure & Modes* viewer.

The list of the Raman-active modes are written in *ira.ldy* file, and the calculated Raman band intensities can be visualized by *Raman Spectrum* viewer. The list of the IR-active modes, their intensities and the values of LO frequencies are written in *iir.ldy* file. The calculated IR intensities can be visualized by *Infrared Spectrum* viewer (Fig. 3).

The third routine fulfills the elastic and piezoelectric constant calculation. These results are also written in the end of *vib.ldy* file.

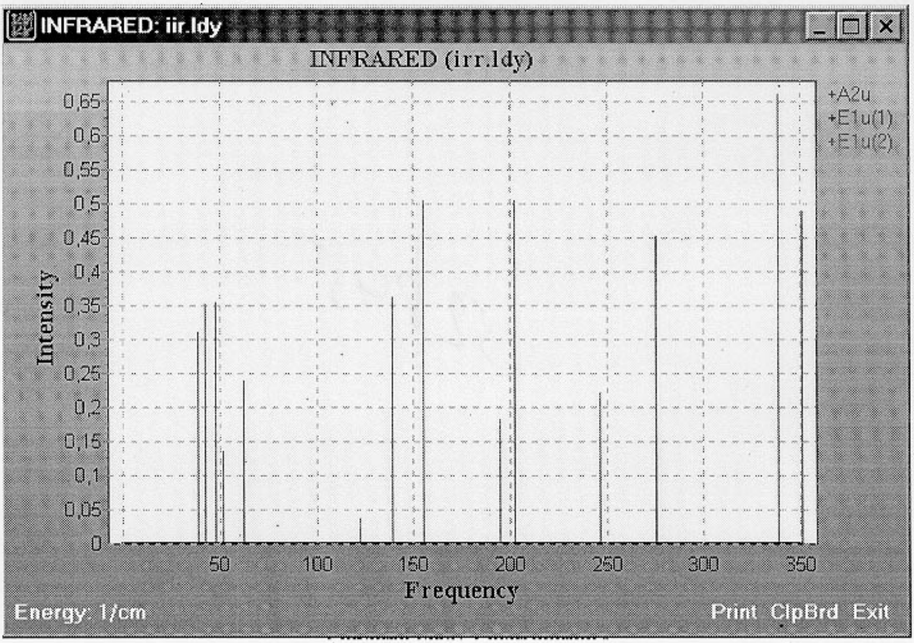


Figure 3. Infrared Spectrum viewer

Frequency differentiation

This auxiliary routine may follow *Optic mode & elasticity*. This routine evaluates the derivatives of the calculated frequencies and elastic constants with respect to the potential model parameters. These data are written in *dif.ldy* file. This is a highly instructive procedure if you intend to fit the calculated frequencies to the experimental data.

Potential energy distribution

This is an auxiliary routine which can follow *Optic mode & elasticity.* It calculates the potential energy distribution – decomposition of the calculated squared frequencies into contributions of different interactions. These data are written in *ped.ldy* file. This a highly instructive procedure if you are interested in a detailed microscopic analysis of the calculated spectrum.

Valence coordinate variation

This is an auxiliary routine which can follow *Optic mode & elasticity.* This programs provides us the eigenvectors in terms of the valence coordinate variation. These data are written in *dql.ldy* file. The list of internal coordinates is taken from the *Valence bonds* section of *cry.ldy* file. This a highly instructive procedure if you would like to thoroughly analyze the calculated vibrational states.

Geometry optimization

This routine serves to find the crystal geometry (atomic positions and the unit cell parameters) which corresponds to zero forces and stresses. This problem is solved by means of Newton method. The second derivatives with respect to the atomic positions are estimated from the calculated normal mode frequencies and eigenvectors. The second derivatives with respect to the unit cell parameters are evaluated from the calculated elastic constants. All this information is taken from *vib.ldy* file. Therefore this routine can be run only after executing of the *Optic mode & elasticity* routine.

This problem involves the optimization of the atomic positions and the unit cell parameters as well. For both the tasks the convergence criterion (the residual force F_{max} and homogeneous stress S_{max}) and the maximal number of iterations (N_i) should be specified.

The routine consists in consequent executing of the atomic positions optimization and unit cell parameter optimization. One can to execute only one type of optimization (with respect to atomic positions or with respect to unit cell parameters). In this case a zero value of the convergence criterion should be assigned to F_{max} or S_{max}, correspondingly.

This routine also enables us to simulate the static equilibrium lattice geometry at finite external pressure P_{ex}. Its value should be given as an input parameter.

Thus, the input data of this routine should include F_{max}, S_{max}, N_i and P_{ex}.

The results of geometry optimization are written in *opx.ldy* file.

Phonon dispersion relations

This routine serves to calculate the phonon dispersion along a chosen line in the Brillouin zone (BZ). If the chosen direction has a specific symmetry, this will be taken into account automatically, and the calculated phonon states line will be assigned according to irreducible representations of the corresponding symmetry subgroup.

The input information for this routine includes two wave vectors (q_1 and q_2) and the number of intervals between them (N).

The calculated phonon frequencies are written in *dsp.ldy* file, and the corresponding curves can be visualized by *Dispersion Curves* viewer (Fig. 4).

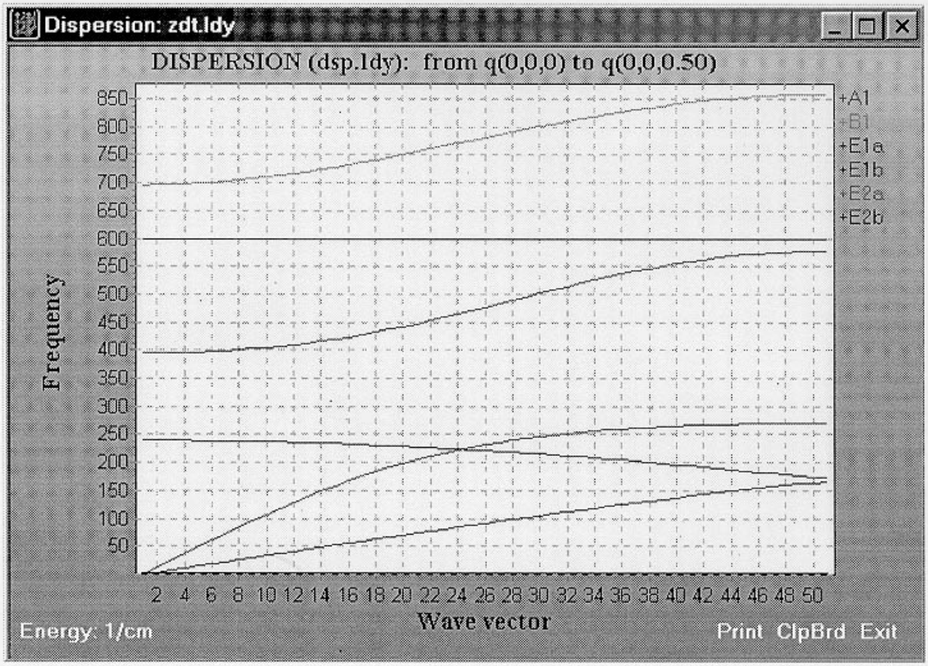


Figure 4. Dispersion Curves viewer

Brillouin zone scanning

This routine serves to calculate the phonon states over the regular wave vector net into the whole BZ. This net includes all the wave vectors

$k = \left(\frac{a^*}{n_1},\frac{b^*}{n_2},\frac{c^*}{n_3}\right)$, at $n_1,n_2,n_3 = -N,\dots,N$.

The symmetry of the lattice is taken into account automatically, and the calculations are carried out only for one of the symmetry equivalent wave vectors.

The only number N should be given in the input data. On choosing this value, be cautious! The total number of wave vectors in the net is equal to $N_t = (2N + 1)^3$, and an unreasonably high N value would lead to a rather voluminous calculation.

The output data (phonon frequencies and eigenvectors) are written in *scn.ldy* file.

Phonon density of states

This routine calculates the phonon density-of-states (DOS), e.g. the frequency distribution of the phonon states. The frequency range from 0 up to ω_{max} is divided onto N intervals, and the corresponding histogram is calculated by scanning over the phonon state data stored in *scn.ldy* file. Besides the total DOS, this routine calculates the partial atomic (weighted with respect to atomic amplitudes) DOS's.

The only number N should be given in the input data.

The results are written in *dos.ldy* file, and the corresponding curves can be visualized by *Phonon Density* viewer (Fig. 5).

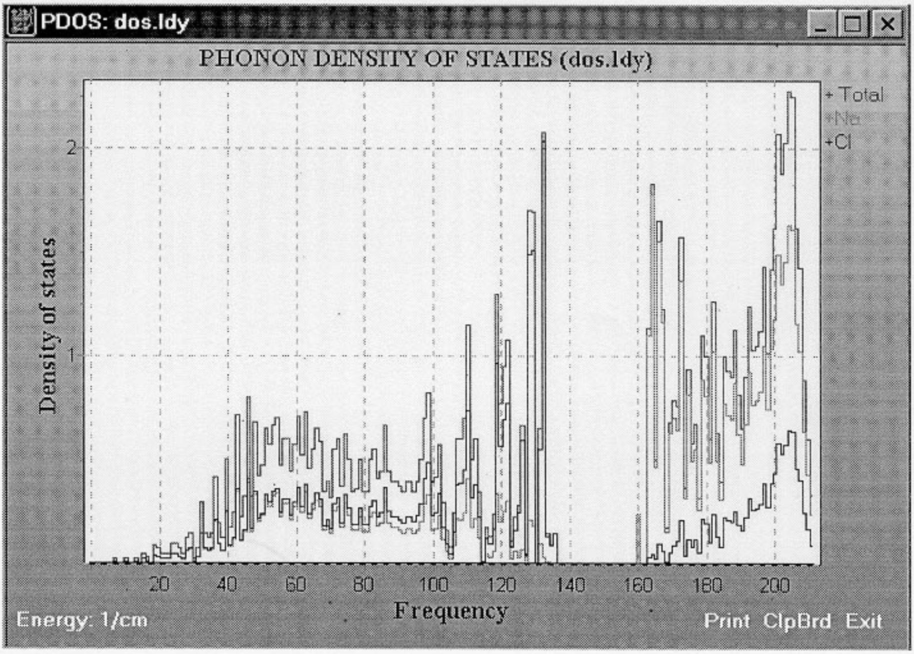


Figure 5. Phonon Density viewer

Atomic thermal parameters

This routine calculates the thermal atomic amplitudes at the given temperature values. These quantities are calculated by scanning over the phonon state data stored in *scn.ldy* file. The input data include the number of T-values (N) and these values (T_1, T_2, ..., T_N). The results are written in *atp.ldy* file.

Pair distribution function

This routine calculates the pair distribution function - the probability distribution of the interatomic distances - from 0 up to R_{max} at the given temperature value. This function is calculated by scanning over the phonon state data stored in *scn.ldy* file. The input data include T and R_{max} values. If it is necessary, this function may be weighted by the neutron or electron scattering cross-section in order to be comparable with the corresponding experimental curves. The results are written in *pdf.ldy* file and the corresponding curve can be visualized by *Pair Distribution function* viewer (Fig. 7).

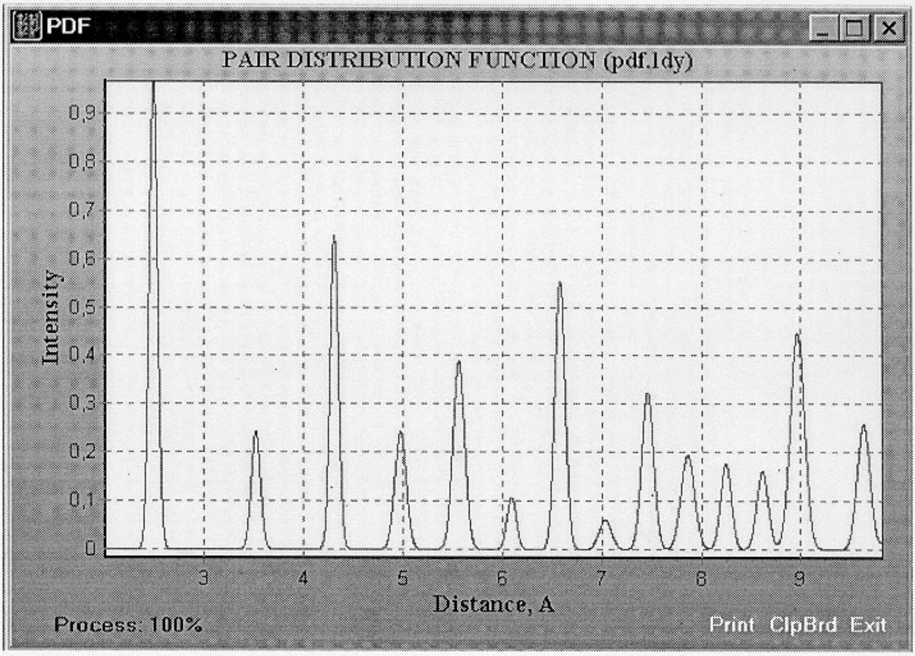


Figure 6. Pair Distribution Function viewer

Thermodynamics

This routine calculates the phonon contribution to the thermodynamic functions (entropy and heat capacity) within the chosen temperature interval. These quantities are calculated by scanning over the phonon state data stored in *scn.ldy* file.

The input data include the number of T-values (N) and these values (T_1, T_2, ..., T_N).

The results are written in *tdm.ldy* file, and the corresponding curves can be visualized by *Thermodynamics* viewer (Fig. 7).

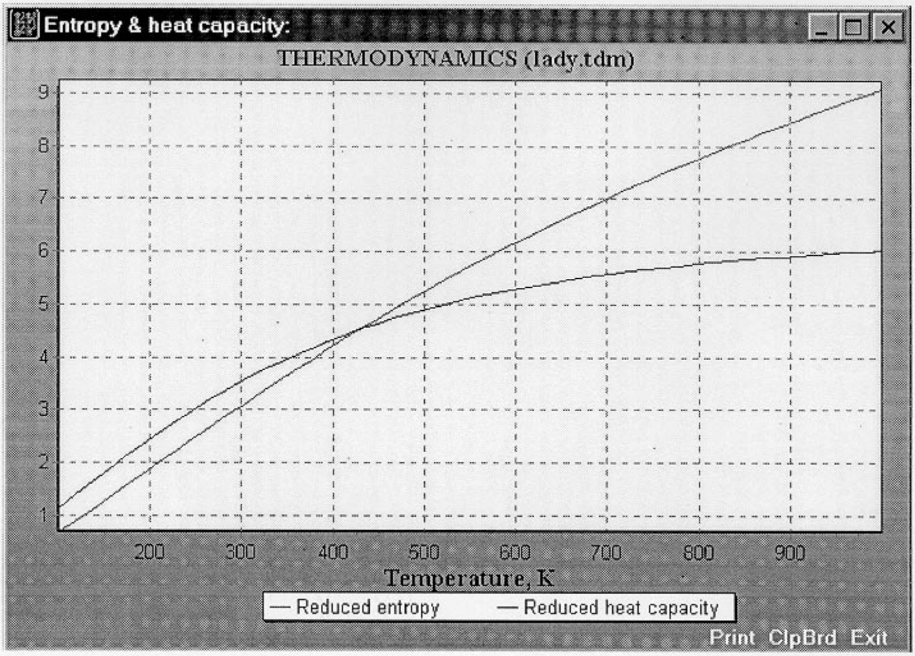


Figure 7. Thermodynamics viewer

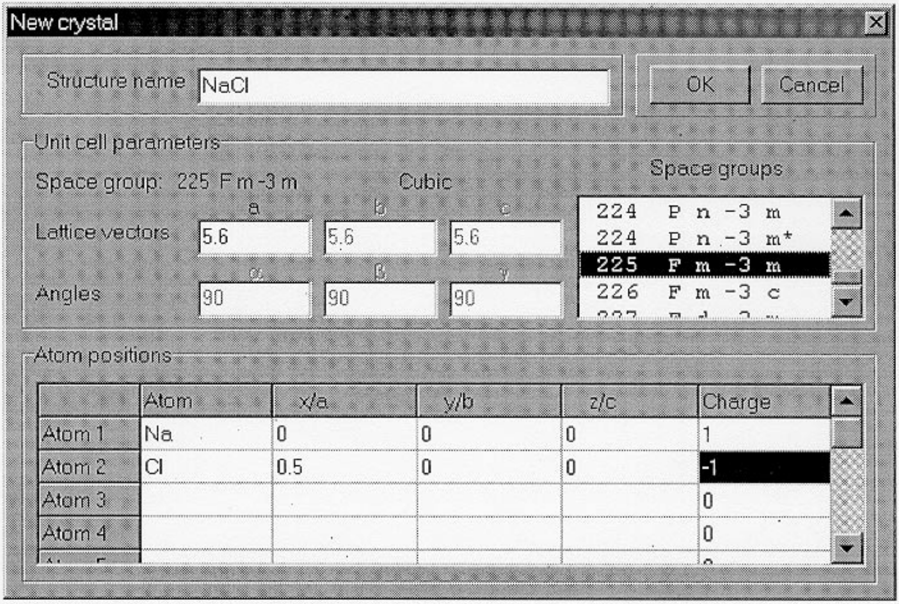
CHAPTER 3
KEYWORDS

Space symmetry group

The space symmetry group should be specified by *Name of group* - the notation given in the International Tables. Within LADY, these notations are chosen to correspond to those of the widely used crystal structure database.

Name of group

is taken to correspond as much as it is possible to the standard notations in the International Tables. One can to look at all the adopted space symmetry groups within *Build New Structure* regime (Fig. 8).



Structure name: NaCl

Space group: 225 F m -3 m Cubic

Lattice vectors: a 5.6, b 5.6, c 5.6

Angles: α 90, β 90, γ 90

Space groups:
224 P n -3 m
224 P n -3 m*
225 F m -3 m
226 F m -3 c

	Atom	x/a	y/b	z/c	Charge
Atom 1	Na	0	0	0	1
Atom 2	Cl	0.5	0	0	-1
Atom 3					0
Atom 4					0

Figure 8. Build New Structure regime

Elementary unit cell

is specified by three cell dimensions *a, b, c* (in Å) and by three angles $\alpha = b\hat{}c$, $\beta = a\hat{}c$, and $\gamma = a\hat{}b$ (in degrees). Take care that the given parameter values should correspond to the chosen crystal symmetry. In all the actual calculations throughout the LADY routines the primitive unit cell is used. If the latter differs from the elementary unit cell, it is determined according to the common convention.

Atomic composition

includes *names of atoms* and the *atomic positions* in the *elementary unit cell.* An additional atomic parameter - atomic charge - should be also given.

Names of atoms

are the three character words. The two first characters must coincide with the standard chemical symbol, e.g. *Ca, Cl* . If the chemical symbol consists of only one character, the underline symbol must be added, e.g. *F_, S_* . The third character is the label of position, e.g. *Ca1, F_a*. If there is only one position occupied by these atoms, the label of position (as well as the underline symbol) can be omitted. For example, the following names of atoms are admitted: *Mg1, F_2, Mg, F,* etc.

Atomic positions

are defined by three numbers which are the partial atomic coordinates in the space of the elementary unit cell vectors $\vec{a},\vec{b},\vec{c}$.

Atomic coordinates

The program applies the space symmetry group transformations in order to generate all the symmetry equivalent atomic positions from the given ones. Thus, the degeneracy of the position is determined, and all the atomic coordinates (partial as well as Cartesian) are written in *cry.ldy* file. The complete *address of the atom* in an infinite regular crystal consists of:

- name of atom,
- number within the symmetry degenerate positions
- 3D unit cell index.

For example the address O_2 [5, 2, 0, -1] corresponds to 5-th of O_2 atoms in the (2,0,-1) unit cell.

Interatomic distances

are written in *cry.ldy* file. The list includes all the distances shorter than 10 Å. The symmetry degeneracy of the distance and corresponding address of atom for a pair of representatives are shown. The first of the atoms is implied to be located within *(0,0,0)* unit cell. So, the record

Ca F_2 1.8772 8 2 4 0 –1 0

denotes that the distance between atoms Ca [2, 0, 0, 0] and F_2 [4, 0, -1, 0] is equal to 1.8772 Å, and there are 8 of such symmetry equivalent pairs of atoms.

Atomic parameters

Different atomic parameters are used within some LADY's routine. They are atomic charge, atomic mass, atomic radius, neutron and x-ray scattering cross-sections. The standard atomic parameter values are taken from *lady.dat* file and are stored in *tab.ldy* file. One can see and edit the content of the *tab.ldy* file by clicking on the corresponding icon.

CHAPTER 4
INPUT

Inp.ldy file

It is strongly recommended to use a separate directory for every project under study.

First of all you must open in this directory the *inp.ldy* file and write there the input information. This can be done automatically within the Build new crystal regime or manually as well. The typical *inp.ldy* could look as follows:

```
FePO4                                  - Name of project
STRUCTURE:                             - An obligatory key line
P 31 21                                - Name of the space symmetry group
5.036  5.036 11.35                     - Unit cell dimensions a,b,c
90 90 120                              - Unit cell angles bc,ac,ab
Fe                                     - Name (i.e. chemical symbol ) of the 1st atom
0.45197 0 0.3333333 1.4 55.8 0.7- Position, charge, mass and radius of the 1st atom
P                                      - 2nd atom
0.4452 0 0.8333333 3.4 0 0             - (the standard mass and radius values will be taken)
O_1                                    - Name (i.e. chemical symbol and label of position) of
                                       the 3rd atom
0.4361 0.3254 0.4 -1.2 0 0
O_2                                    - 4th atom
0.40888  0.2597 0.8793 -1.2  0  0
end                                    - Key line
POTENTIAL:                             - Key line
IAP                                    - Inter- Atomic Potential contribution
Fe    O_*  EXP
0  20   3200  0.216
Fe    O_*  POW
0  20   -30   6
P     O_*  EXP
0  20  1447.5 0.19264
P      O_*  POW
0  20  -3.2   6
O_*  O_*  EXP
0  20  222.48 0.36232
O_*  O_*  POW,
0  20 -28.035  6
end                                    - Key line

VFF                                    - Valence Force Field contribution
O_1 Fe   P
1  0  0  0  3  0  0  0
0.2 , 0.1,  0.1,  0.2
O_2 Fe   P
3  0  0  1  1  0  0  0
0.15,  0.11, 0.1, 0.2
end                                    - Key line
```

```
SHM                                 - Shell Model contribution
O_1
-2.7, 1.2, 0, 0
O_2
-2.7, 1.2, 0, 0
end                                 -Key line
END                                 -Key line
```

IAP input

begins with the key line «IAP» and finishes by the key line «end». Between them the definition of the pair-wise potentials is written. This consists of two lines for every potential. The first line consists of three 3-character words:
name of first atom, name of second atom, type of interaction
In the second line the four numeric values are given:
R_{min}, R_{max}, a, b
here R_{min} and R_{max} are the minimal and maximal radii of interaction, a and b are two potential parameters. For example, the record

```
Fe  O_1  EXP
0  20   3200  0.216
```

corresponds to the potential $\phi(r)=3200\exp(-r/0.216)$, which acts between atoms Fe and O_1 within $0 < r < 20$.

Several standard analytic expressions for $\phi(r)$ are available in LADY. All of them involve two parameters a and b. These standard functions as well as the corresponding parameter units are listed in the table:

Description	***Type***	***Expression***	***a unit***	***b unit***
Born-Karman model	BKM	$A = a, B = b$	aJ/Å^2	aJ/Å^2
Harmonic function	HAR	$\frac{1}{2}a(r-b)^2$	aJ	Å
Exponent function	EXP	$a\exp\left(-\frac{r}{b}\right)$	aJ	Å
Power function	POW	ar^{-b}	aJ/Å^b	-
Coulomb low	COU	$\frac{ab}{r}$	e	E

If you want to use the same potential for all the chemically equivalent atoms in different crystal positions, then you should write asterisk (*) in the third position of atom name. So, the record

```
Fe  O_*  EXP
0  20   3200  0.216
```

is equivalent to the combination

```
Fe  O_1  EXP
0  20   3200  0.216
Fe  O_2  EXP
0  20   3200  0.216.
```

VFF input

begins with the key line «VFF» and finishes by the key line «end». Between them the definition of the valence coordinates and values of corresponding force constants are written. This consists of three lines for every valence coordinate.

The first line consists of two-character words for every valence bond:
name of first atom, name of second atom,

or of three 3-character words for every valence angle:
name of first (central) atom, name of second atom, name of third atom

In the second line the address of the second and third atoms are given (the address of the first atom is always implied to be [1, 0, 0, 0]).

In the third line the four numeric values are given:

$$F_{nn}=\frac{d^2V}{ds_n^2},\; Z_n=\frac{dp_n}{ds_n}\;;\; E_n^1=\frac{d\varepsilon_n^1}{ds_n},\; E_n^2=\frac{d\varepsilon_n^2}{ds_n}$$

for valence bond, and correspondingly

$$F_{nn}=\frac{d^2V}{db_n^2},\; H_n=\frac{d^2V}{ds_n^1ds_n^2},\; A_n^1=\frac{d^2V}{db_nds_n^1},\; A_n^2=\frac{d^2V}{db_nds_n^2}$$

for valence angle.

For example, the record

```
Fe  O_1
1   0  0  0
0.5 , 0.1,  0.2,  0.3
```

corresponds to the valence bond Fe (1 0 0 0) - O_1 (1 0 0 0),
and the parameters
$F_{22}, H_2, A_2^1, A_2^2$

whereas, the record

```
O_1 Fe  P
1   0  0  0   3   0  0  0
0.5 , 0.1,  0.2,  0.3
```

corresponds to the valence angle Fe (1 0 0 0) - O_1 (1 0 0 0) - P (3 0 0 0), and the force constants $F_{22}, H_2, A_2^1, A_2^2$

PIM and SM input

begins with the key line «PIM» or «SM» and finishes by the key line «end». Between them the definition of the atomic polarizability parameters are written. This consists of two lines for every polarizable atom.

The first line consists of one 3-character word:

name of atom

In the second line the four numeric values are given:

shell charge, α_{xx}, α_{yy} , α_{zz}

here α_{xx}, α_{yy} *and* α_{zz} are the components of the atomic polarizability tensor. The latter may be set different in order to take into account the crystal anisotropy.

The shell charge value is not used within PIM model, so it can be set arbitrarily.

There is an example of the SM input data:

```
SHM
O_1
-2.7, 1.2, 1.2, 1.2
O_2
-2.7, 1., 1., 1.
end
```

RIM input

does not need any additional data. The atomic charges are taken from the atomic composition section.

The basic units used in LADY

Length	– Å
Energy	– aJ (1 aJ =10^{-18}J = 1 mdyn·Å)
Mass	– a.m.u. (1 a.m.u. = $1.660056 \cdot 10^{-27}$ kg)
Charge	– *e* (1 *e* = $1.60211 \cdot 10^{-19}$C; 1 e^2/Å = 2.306 aJ)
Frequency	– cm^{-1} (1 cm^{-1} =1 aJ/Å/a.m.u.= $1.6973 \cdot 10^{6}$ cm^{-2})
Pressure	– GPa (1 GPa = 10^{-3} aJ/Å^3 = 10 kbar = 0.01 Mbar)
Elastic constants	– GPa (1 GPa = 10^{-3} aJ/Å^3 = 10 kbar = 0.01 Mbar)
Bulk module	– GPa (1 GPa = 10^{-3} aJ/Å^3 = 10 kbar = 0.01 Mbar)

LIMITATIONS

The present version has the following limits:
Atoms in the unit cell – 100, if RGM option is not used
Atoms in the unit cell – 300, if RGM option is used *)
Rigid Molecules – 50 *)
IAP terms – 100
VFF terms – 100
Valence bonds – 1000
Valence angles – 1000
DOS, ATP, TDM points – 1000

*) The true limitation is the number of degrees of freedom (DF), which determines the dimension of the dynamic matrix. Each free atom has 3 DF, whereas each rigid molecule has 6 DF. So, the exact limits is determined as $3N_i+6N_m<300$, where N_i is the number of the free atoms and N_m is the number of the rigid molecules.

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Смирнов М.Б., Казимиров В.Ю. E14-2001-159
LADY: программа для моделирования динамики решетки

Программа LADY позволяет моделировать различные свойства кристаллов в зависимости от адиабатической потенциальной функции, такие как
— равновесную кристаллическую структуру,
— динамические свойства,
— инфракрасные спектры и спектры комбинационного рассеяния,
— термодинамические свойства — зависимость от температуры и давления кристаллической структуры и всех вышеперечисленных динамических свойств.

LADY позволяет использовать большинство широко распространенных потенциальных моделей.

LADY автоматически проводит симметрийный анализ кристаллической структуры и фононных состояний.

LADY применима для кристаллов произвольного химического состава и пространственного строения.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 2001

Smirnov M.B., Kazimirov V.Yu. E14-2001-159
LADY: Software for Lattice Dynamics Simulations

This program LADY is capable of simulating different crystal properties depending on the adiabatic potential function such as:
— equilibrium crystal structure;
— dynamical properties — phonon states, elastic and piezoelectric constants;
— IR, Raman spectra;
— thermodynamic properties — temperature and pressure dependence of the crystal structure and of all the above mentioned dynamical properties.

LADY incorporates many widely used potential models.

LADY accomplishes an automatic account of the symmetry for the crystal structure and for the phonon states as well.

LADY is applicable for a crystal of arbitrary chemical and spatial constitution.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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Макет Н.А.Киселевой

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