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# *NEUTRON*: a program for computing phonon extinction rules of inelastic neutron scattering and thermal diffuse scattering experiments

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*NEUTRON* is a computer program for calculating the phonon extinction rules for inelastic neutron scattering experiments. Given the space group and the phonon symmetry specified by the wavevector, the program examines the inelastic neutron scattering activity of the corresponding phonons for all possible types of scattering vectors. The systematic selection rules are also useful in the interpretation of the results of thermal diffuse scattering. *NEUTRON* forms part of the Bilbao Crystallographic server (http://www.cryst.ehu.es) and can be used *via* the Internet from any computer with a Web browser.

## 1. Introduction

Both inelastic neutron scattering (INS) data and thermal diffuse scattering (TDS) data are a rich source of lattice dynamical information. However, a proper interpretation of the results requires additional information on the symmetry of the phonon modes. An additional obstacle in the case of TDS is the essentially integral character of the phenomena: there are a large number of wavevectors $\mathbf{q}$ distributed throughout the Brillouin zone which may contribute to the TDS intensities. However, a quantitative account of the INS and TDS data could be facilitated by the use of systematic mode extinctions.

The existence of general phonon symmetry-extinction rules in inelastic neutron scattering experiments has been recently demonstrated: the resulting phonon absences depend only on the mode symmetry and the scattering vector $\mathbf{Q}$, and not on the specific atomic positions of the crystal structures (Perez-Mato *et al.*, 1998). Using the distribution of the reciprocal-lattice vectors (Brillouin zones) into types with respect to the symmetry group of the scattering vector, it is possible to show that Brillouin zones belonging to the same type are characterized by the same set of selection rules. The derived extinction rules prove to be very useful for the identification of the symmetries of the measured phonons, and their systematic use helps the optimization of INS experiments (Aroyo *et al.*, 2002*a*). These selection rules also apply to phonon X-ray inelastic scattering, and their use has been successfully extended to TDS studies (Aroyo *et al.*, 2002*b*).

The aim of the present contribution is to report on the development of a systematic procedure for the calculation of phonon extinction rules. An algorithm based on this procedure serves as the basis of the computer program *NEUTRON*. Given the space group and the symmetry of the phonon, specified by the wavevector $\mathbf{q}$, the program examines the INS activity of the $\mathbf{q}$ phonons for all different types of scattering vectors.

## 2. Mathematical background

The one-phonon scattered neutron intensity due to $n$ degenerate modes of wavevector $\mathbf{q}$ and measured at a particular scattering vector $\mathbf{Q}$ (here $\mathbf{Q} = \mathbf{H} - \mathbf{q}$, with $\mathbf{H} \in \mathbf{L}^*$, a reciprocal-lattice vector) is proportional to $\sum_{j=1}^{n} |F_j(\mathbf{Q})|^2$, where $F_j(\mathbf{Q})$ is the one-phonon dynamical structure factor for inelastic scattering (see *e.g.* Squires, 1978):

$$F_j(\mathbf{Q}) = \sum_{\alpha=1}^{s} (b_\alpha / m_\alpha^{1/2})[\mathbf{e}(\alpha|\mathbf{q}, \tau j) \cdot \mathbf{Q}] \exp(i\mathbf{Q} \cdot \mathbf{r}_\alpha) \times \exp[-W_\alpha(\mathbf{Q})]. \quad (1)$$

Here, the index $\alpha$ labels the atoms in the unit cell, $m_\alpha$ is the mass of the atom $\alpha$, $b_\alpha$ its coherent scattering length and $W_\alpha(\mathbf{Q})$ the corresponding Debye–Waller factor. The polarization vectors $\mathbf{e}(\alpha|\mathbf{q}, \tau j)$, $j = 1, \ldots, n$ of the $\mathbf{q}$-vector modes transform according to the $n$-dimensional irreducible representation $\boldsymbol{D}^{\mathbf{q},\tau}$ of the little group $\mathcal{G}^{\mathbf{q}}$ of the wavevector.

The INS selection rules are derived using the transformation properties of the dynamical structure factors $F_j(\mathbf{Q})$ under the elements $W^{\mathbf{q}} = (\boldsymbol{W}^{\mathbf{q}}, \boldsymbol{w}^{\mathbf{q}})$ of the little group $\mathcal{G}^{\mathbf{q}}$ (Perez-Mato *et al.*, 1998; Aroyo *et al.*, 2002*b*). Taking into account the fact that the set of polarization vectors $\{\mathbf{e}(\alpha|\mathbf{q}, \tau j), j = 1, n\}$ spans a carrier space of an irreducible representation $\boldsymbol{D}^{\mathbf{q},\tau}$ of the little group $\mathcal{G}^{\mathbf{q}}$, it is straightforward to show that the dynamical structure factors [equation (1)] satisfy the equation

$$F_j^\tau(\mathbf{Q}\boldsymbol{W}^{\mathbf{q}}) = \textstyle\sum_{k=1}^{n} \boldsymbol{D}^{\mathbf{q},\tau}(\boldsymbol{W}^{\mathbf{q}}, \boldsymbol{w}^{\mathbf{q}})_{kj} \exp(-i\mathbf{Q} \cdot \boldsymbol{w}^{\mathbf{q}}) F_k^\tau(\mathbf{Q}). \quad (2)$$

Obviously, the transformation properties of the dynamical structure factors are determined by the irreducible representation $\boldsymbol{D}^{\mathbf{q},\tau}$ of the corresponding phonon. The additional upper index of the structure-factor symbol, $F_j^\tau(\mathbf{Q})$ [used in equation (2) and henceforth], is to emphasize this fact.

The basic result, equation (2), induces two types of relations.

(i) *Relations between dynamical structure factors* belonging to scattering vectors equivalent under $\boldsymbol{W}^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{q}}$, where $\overline{\mathcal{G}}^{\mathbf{q}}$ is the point group of $\mathcal{G}^{\mathbf{q}}$ (or the little co-group). Equation (2) implies the expected result $\sum_{j=1}^{n} |F_j^\tau(\mathbf{Q})|^2 = \sum_{j=1}^{n} |F_j^\tau(\mathbf{Q}\boldsymbol{W}^{\mathbf{q}})|^2$, *i.e.* equal scattering intensities for equivalent scattering vectors.

(ii) *Systematic absences*. The elements $\boldsymbol{W}^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{q}}$ satisfying the condition $\mathbf{Q}\boldsymbol{W}^{\mathbf{q}} = \mathbf{Q}$, form the so-called *strict point group*, $\overline{\mathcal{G}}^{\mathbf{Q}}$, of the scattering vector $\mathbf{Q}$. For the $\boldsymbol{W}^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{Q}}$, equation (2) reduces to

$$F_j^\tau(\mathbf{Q}) = \textstyle\sum_{k=1}^{n} \boldsymbol{T}^{\mathbf{Q},\tau}(\boldsymbol{W}^{\mathbf{q}})_{kj} F_k^\tau(\mathbf{Q}), \quad (3)$$

where the matrices

$$T^{\mathbf{Q},\tau}(W^{\mathbf{q}}) = D^{\mathbf{q},\tau}(W^{\mathbf{q}}, w^{\mathbf{q}}) \exp(-i\mathbf{Q} \cdot w^{\mathbf{q}}) \quad (4)$$

form a representation, reducible in the general case, of the strict point group $\overline{\mathcal{G}}^{\mathbf{Q}}$.

A set of non-zero values of $F_j^{\tau}(\mathbf{Q})$ can fulfil equation (3) if the representation $T^{\mathbf{Q},\tau}$ contains the identity representation of $\overline{\mathcal{G}}^{\mathbf{Q}}$. Hence, one can formulate the following theorem on INS activity (Perez-Mato *et al.*, 1998).

*INS Theorem*. All phonon modes of wavevector **q** and symmetry given by the small irreducible representations $D^{\mathbf{q},\tau}$ are INS inactive at a scattering vector **Q**, if the representation $T^{\mathbf{Q},\tau}$ [equation (4)] of $\overline{\mathcal{G}}^{\mathbf{Q}}$ does not contain the identity representation.

The above result equally holds for inelastic X-ray scattering or X-ray diffuse scattering and it can be used, for example, for the study of thermal diffuse scattering activity of phonon modes at a scattering vector **Q** (Aroyo *et al.*, 2002*a*). It should be noted that the derived extinction rules are not restricted to inelastic scattering only, but apply also to elastic scattering in the cases where the disorder can be described by certain phonon-like static displacements.

## 3. Procedure for the calculation of phonon selection rules

Given a phonon wavevector **q** and a scattering vector **Q**, the procedure consists essentially of constructing the representation $T^{\mathbf{Q},\tau}$ of $\overline{\mathcal{G}}^{\mathbf{Q}}$, and checking if the identity representation is among the irreducible constituents of its decomposition. The main steps are as follows.

### 3.1. Little-group irreducible representations of $\mathcal{G}^{\mathbf{q}}$

Given the wavevector **q**, the little group $\mathcal{G}^{\mathbf{q}}$ and the corresponding little-group irreducible representations $D^{\mathbf{q},j}$ are determined. The little group $\mathcal{G}^{\mathbf{q}}$ is a subgroup of the space group $\mathcal{G} = \{(W, w)\}$ whose elements $W^{\mathbf{q}} = (W^{\mathbf{q}}, w^{\mathbf{q}})$ are defined by the conditions

$$\mathcal{G}^{\mathbf{q}} = \{(W, w) \in \mathcal{G} | \mathbf{q}W = \mathbf{q} + \mathbf{H}, \mathbf{H} \in \mathbf{L}^*\}. \quad (5)$$

The irreducible representations of the little group are well known and treated in many books on representation theory (for example, see Bradley & Cracknell, 1972, and the references therein).

### 3.2. Distribution of the set of Q vectors into types

For a given phonon wavevector **q**, the set of all possible scattering vectors, **Q** = **H** − **q**, form an infinite set. However, it is possible to partition the **Q** set first into **Q** vector orbits and then into **Q** vector types. This classification allows an efficient procedure for the study of the phonon selection rules as each **Q** vector type is characterized by the same set of selection rules. It is then sufficient to study the extinctions for one representative of each of the **Q** vector types.

The symmetry operations of the little co-group $\overline{\mathcal{G}}^{\mathbf{q}}$ partition the set of all **Q** vectors into classes of symmetrically equivalent scattering vectors. The finite set of all images $\{\mathbf{Q}_o W^{\mathbf{q}}\}$ of $\mathbf{Q}_o$ under the symmetry operations $W^{\mathbf{q}}$ is called the orbit of $\mathbf{Q}_o$ under $\overline{\mathcal{G}}^{\mathbf{q}}$. These orbits are disjoint, as they either have no element in common or are identical; thus each scattering vector belongs to exactly one orbit.

The set of all symmetry operations of the little co-group that leave a **Q** vector invariant forms its strict point group $\overline{\mathcal{G}}^{\mathbf{Q}}$ with respect to $\overline{\mathcal{G}}^{\mathbf{q}}$:

$$\overline{\mathcal{G}}^{\mathbf{Q}} = \{W^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{q}} | \mathbf{Q}W^{\mathbf{q}} = \mathbf{Q}\}. \quad (6)$$

With respect to $\overline{\mathcal{G}}^{\mathbf{Q}}$ two types of **Q** vectors are to be distinguished. A **Q** vector is called *general* with respect to $\overline{\mathcal{G}}^{\mathbf{q}}$ if there is no symmetry operation of $\overline{\mathcal{G}}^{\mathbf{q}}$ (apart from the identity) that leaves the **Q** vector invariant, *i.e.* the order of $\overline{\mathcal{G}}^{\mathbf{Q}}$ equals 1, $|\overline{\mathcal{G}}^{\mathbf{Q}}| = 1$. A *special* **Q**-vector is characterized by a strict point group whose order $|\overline{\mathcal{G}}^{\mathbf{Q}}| > 1$.

Each **Q** vector of a $\overline{\mathcal{G}}^{\mathbf{q}}$ orbit has a strict point group $\overline{\mathcal{G}}^{\mathbf{Q}}$ which is a subgroup of $\overline{\mathcal{G}}^{\mathbf{q}}$. The strict point groups of **Q** vectors belonging to the same orbit are conjugate (*i.e.* symmetrically equivalent) subgroups of $\overline{\mathcal{G}}^{\mathbf{q}}$. They are of the same order and the index of (any) $\overline{\mathcal{G}}^{\mathbf{Q}}$ in $\overline{\mathcal{G}}^{\mathbf{q}}$ determines the length of the orbit.

The classification of the $\overline{\mathcal{G}}^{\mathbf{q}}$ orbits into types is done by comparing the sets of strict point groups assigned to each orbit: two orbits belong to the same type of scattering vectors if their complete sets of strict point groups are identical.

### 3.3. INS selection rules of the Q vector types

Once the little-group irreducible representations $D^{\mathbf{q},\tau}$ are determined, the matrices of the representation $T^{\mathbf{Q},\tau}$ of the strict point group $\overline{\mathcal{G}}^{\mathbf{Q}}$ are constructed directly from equation (4). A **q** phonon, with a symmetry given by $D^{\mathbf{q},\tau}$, is INS inactive if the following condition is satisfied:

$$\sum_{W^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{Q}}} \chi^{\mathbf{q},\tau}(W^{\mathbf{q}}, w^{\mathbf{q}}) \exp(-i\mathbf{Q} \cdot w^{\mathbf{q}}) = 0. \quad (7)$$

Here, $\chi^{\mathbf{q},\tau}(W^{\mathbf{q}}, w^{\mathbf{q}})$ are the characters of the representation $D^{\mathbf{q},\tau}$ of $\mathcal{G}^{\mathbf{q}}$. Obviously, there are non-trivial symmetry restrictions on the INS phonon activity for special **Q** vectors only. If $\overline{\mathcal{G}}^{\mathbf{Q}}$ contains the identity operation only, *i.e.* a general **Q** vector, then all symmetry types of **q** phonons can be INS active.

## 4. Implementation

The algorithm of the computer program *NEUTRON* follows the main steps of the procedure for the calculation of the extinction rules.

In the *input* block the user is expected to provide the data for the space group $\mathcal{G}$ and the phonon wavevector **q**. The space group is specified by its consecutive number as given in *International Tables for Crystallography*, Vol. A (2002, hereinafter referred to as ITA), and the default space-group settings used by the program correspond to the conventional ones used in ITA. In the cases with more than one conventional setting, the following choice is made: unique-axis-*b* settings for the monoclinic groups, hexagonal-axes settings for the rhombohedral groups and origin-2 choice for the centrosymmetric groups. It is also possible to carry out the calculations for a non-conventional setting of $\mathcal{G}$. In this case the user is expected to provide the transformation matrix defining the relation to the default ITA setting.

The **q** vector coefficients could be referred to the primitive basis of the reciprocal space as found, for example, in Cracknell *et al.* (1979). Another possibility for the cases of centred lattices is to define the wavevector with respect to centred bases of reciprocal space, dual to the conventional ITA settings. There is also an option for wavevector coordinates with respect to a coordinate system which is dual to the non-conventional setting defined by the user. An online wavevector database (KVEC) with figures of representation domains, Brillouin zones and classification tables of the wavevectors for all 230 space groups is also available on the Bilbao Crystallographic server (http://www.cryst.ehu.es).

The *output* of the program consists of three main blocks: space-group data block, **q** vector data block including the little-group irreducible representations, and the data block with **Q** vector types and extinction rules.

*Space-group data.* The listed data start with the ITA number of the space group and its lattice type. Then follows the set of non-trans-

**Table 1**
Little co-group irreducible representations of the space groups *Pmmm* and *Pnma* for $\mathbf{q} = \mathbf{\Gamma}$, and for $\mathbf{q} = \mathbf{Y}$ of the space group *Cmmm*.

The irreducible-representation matrices (which coincide with the characters, as all irreducible representations are one-dimensional) are listed for the generators of the little co-group $\mathcal{G}^{\Gamma}$ (or $\mathcal{G}^{\mathbf{Y}}$).

| | Irreducible representations | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Generators | Γ1<br>Y1 | Γ2<br>Y2 | Γ3<br>Y3 | Γ4<br>Y4 | Γ5<br>Y5 | Γ6<br>Y6 | Γ7<br>Y7 | Γ8<br>Y8 |
| $2_z$ | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 |
| $2_y$ | 1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 |
| $\bar{1}$ | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 |

**Table 2**
Selection rules for **Γ** phonons for space groups *Pmmm* and *Pnma*.

The symmetry types (irreducible representations) of phonons which can be INS active (allowed) are listed for a representative $\mathbf{H}(h, k, l)$ of a Brillouin zone class (*n* integer). The groups $\overline{\mathcal{G}}^{\mathbf{Q}}$ are given as oriented site-symmetry symbols. For the irreducible-representation labels, see Table 1.

| | **Γ** phonons, $\overline{\mathcal{G}}^{\Gamma} = mmm$, $\mathbf{Q} = \mathbf{H}$ | | |
|---|---|---|---|
| | | INS-active types of phonons | |
| Brillouin zone | $\overline{\mathcal{G}}^{\mathbf{Q}}$ | *Pmmm* | *Pnma* |
| $\mathbf{H}(0, 0, 0)$ | *mmm* | Γ1 | Γ1 |
| $\mathbf{H}(0, 0, l)$<br>$h \neq 0$ | *mm*2 | Γ1, Γ4 | $l = 2n$: Γ1, Γ4<br>$l = 2n + 1$: Γ5, Γ8 |
| $\mathbf{H}(0, k, 0)$<br>$k \neq 0$ | *m*2*m* | Γ1, Γ6 | $k = 2n$: Γ1, Γ6<br>$k = 2n + 1$: Γ3, Γ8 |
| $\mathbf{H}(h, 0, 0)$<br>$h \neq 0$ | 2*mm* | Γ1, Γ8 | $h = 2n$: Γ1, Γ8<br>$h = 2n + 1$: Γ4, Γ5 |
| $\mathbf{H}(h, k, 0)$<br>$h, k \neq 0$ | ..*m* | Γ1, Γ3, Γ6, Γ8 | $h = 2n$: Γ1, Γ3, Γ6, Γ8<br>$h = 2n + 1$: Γ1, Γ4, Γ5, Γ7 |
| $\mathbf{H}(h, 0, l)$ | .*m*. | Γ1, Γ4, Γ5, Γ8 | Γ1, Γ4, Γ5, Γ8 |
| $\mathbf{H}(0, k, l)$<br>$h, k \neq 0$ | *m*.. | Γ1, Γ4, Γ6, Γ7 | $h + k = 2n$: Γ1, Γ4, Γ6, Γ7<br>$h + k = 2n + 1$: Γ2, Γ3, Γ5, Γ8 |

lation generators used by the program for the construction of the matrix-column pairs of the coset representatives of the group $\mathcal{G}$ with respect to its translation subgroup. Both the generators and the coset representatives are listed in a $(3 \times 4)$ matrix form.

**q** *vector data*. The wavevector block starts with the information on the **q** vector coordinates given by the user. For its calculations the program uses wavevector coordinates referred to a coordinate system of the reciprocal space which is dual to the default conventional settings of $\mathcal{G}$. The translational coset representatives of the little group $\mathcal{G}^{\mathbf{q}}$ are listed as matrix-column pairs in a $(3 \times 4)$ matrix form. The module *REPRES* calculates the little-group irreducible representations by applying an induction procedure from the allowed representations of *P*1. The matrices of $\boldsymbol{D}^{\mathbf{q},\tau}$ are listed for all translational coset representatives of the little group $\mathcal{G}^{\mathbf{q}}$ in a consecutive order. The matrix coefficients (in general complex) are given in the polar form (modulus and phase angle). The labels of the irreducible representations consist of the wavevector letter(s) and a consecutive number determined by the order of the irreducible-representation generation by *REPRES*.

**Q** *vector types and extinction rules*. The next step is the distribution of the set of scattering vectors **Q** into types and the determination of the corresponding strict point groups. The action of each little co-group element $\boldsymbol{W}^{\mathbf{q}}$ on the set of scattering vectors $\mathbf{Q} = \mathbf{H} - \mathbf{q}$, implying the strict point group condition [equation (6)], results in a set of restrictions on the values of the $h, k, l$ components of the lattice vector **H**. Different sets of restrictions correspond to different types of scattering vectors which are further characterized by their strict point groups. Given a **Q** vector type, the INS phonon activity condition [equation (7)] is checked and listed for all phonon symmetries (*i.e.* irreducible representations $\boldsymbol{D}^{\mathbf{q},\tau}$ of the little group). A symmetry type of phonon is considered as INS active (allowed) if the sum over all little co-group elements in equation (7) gives a non-zero integer.

## 5. Technical details

*NEUTRON* is a command-line based program written in C++ and can be used under any operating system that has a standard C++ compiler, such as Microsoft Windows, Linux or UNIX-like (although for now there are makefiles only for GNU C++ and Borland Free Compiler 5.5).

The program requires not more than several megabytes of RAM, depending on the dimension of the little-group representations. The software package that includes *NEUTRON* along with some additional crystallographic programs occupies not more than 10 Mbyte disk space. However, the program can be used without local installation from any computer with a Web browser.

## 6. Examples

### 6.1. Example 1

As an example we will consider the extinctions for phonons of the **Γ** point [$\mathbf{q} = (0, 0, 0)$] for the space groups *Pmmm* and *Pnma*.

The input consists of the ITA numbers of both groups (No. 47 for *Pmmm* and No. 62 for *Pnma*) and the **q** vector data. The space-group data block of the output contains the list of the non-translational generators as chosen in the ITA. For example, in the case of *Pnma* this set is $\langle (2_z \mid \frac{1}{2}, 0, \frac{1}{2}), (2_y \mid 0, \frac{1}{2}, 0), (\bar{1} \mid 0, 0, 0) \rangle$ [shown in the form of $(3 \times 4)$ matrices]. The sets of eight translational coset representatives for the two groups correspond to the 'general position' lists of the ITA. The wavevector data block starts with the **q** vector coordinates followed by a list of the translational coset representatives of the little group. As the wavevector we are considering is **Γ**, $\mathcal{G}^{\Gamma}$ coincide with the space groups *Pmmm* and *Pnma* and the eight little-group irreducible representations for both cases are simply related to the irreducible representations of the point group *mmm* (Table 1).

The results listed in the data block on the **Q** vector types and extinctions rules are summarized in Table 2. The space groups *Pmmm* and *Pnma* belong to the arithmetic crystal class *mmmP*, so the distribution of the **Q** vectors first into orbits and then into **Q** vector types is the same.[1] There are seven non-trivial **Q** vector types, represented by the corresponding Brillouin zone vectors **H**. The strict point groups $\overline{\mathcal{G}}^{\mathbf{Q}}$ refer to the orbit representatives, which are listed.

In the case of *Pmmm* the origin of the selection rules for different **Q** vectors is easily traced due to the simple one-dimensional irreducible representations $\boldsymbol{D}^{\Gamma,\tau}$ (Table 1) and the fact that all factors $\exp(-i\mathbf{H} \cdot \boldsymbol{w}^{\mathbf{q}})$ [equation (4)] equal 1. To obtain the selection rules it is just necessary to consider the subduction of the little-group irreducible representations to the strict point group (in our case $\overline{\mathcal{G}}^{\mathbf{Q}} = \overline{\mathcal{G}}^{\mathbf{H}}$). For example, the strict point group of $\mathbf{H}(0, 0, l)$ is $2mm = \{1, 2_z, m_y, m_x\}$. The reference to the irreducible representation characters of Table 1 shows that only two irreducible representations

[1] In fact, this distribution is valid for all 16 orthorhombic groups from the arithmetic crystal class *mmmP*.

**Table 3**
Selection rules for **Y** phonons, space group *Cmmm*.

The symmetry types (irreducible representations) of phonons which can be INS active (allowed) are listed for a representative **H**($h$, $k$, $l$) of a Brillouin zone class ($n$ integer). The groups $\overline{\mathcal{G}}^{\mathbf{Q}}$ are given as oriented site-symmetry symbols. For the irreducible-representation labels, see Table 1.

| Brillouin zone | | **Y** phonons, $\overline{\mathcal{G}}^{\mathbf{Y}} = mmm$, $\mathbf{Q} = \mathbf{H} - \mathbf{Y}$ | |
|---|---|---|---|
| **Y**(1, 0, 0) | **Y**(0, 1, 0) | $\overline{\mathcal{G}}^{\mathbf{Q}}$ | INS-active types of phonons |
| **H**($h$, 0, 0) $h = 2n$ | **H**($h$, 1, 0) $h = 2n + 1$ | $2mm$ | Y1, Y8 |
| **H**(1, $k$, 0) $k = 2n + 1$ | **H**(0, $k$, 0) $k = 2n$ | $m2m$ | Y1, Y6 |
| **H**($h$, $k$, 0) $h + k = 2n$ | **H**($h$, $k$, 0) $h + k = 2n$ | $..m$ | Y1, Y3, Y6, Y8 |
| **H**($h$, 0, $l$) $h = 2n$ | **H**($h$, 1, $l$) $h = 2n + 1$ | $.m.$ | Y1, Y4, Y5, Y8 |
| **H**(1, $k$, $l$) $k = 2n + 1$ | **H**(0, $k$, $l$) $k = 2n$ | $m..$ | Y1, Y4, Y6, Y7 |

**Table 4**
Little co-group irreducible representations of the space group *Cmmm* for **q** = **Δ**.

The irreducible-representation matrices (which coincide with the characters, as all irreducible representations are one-dimensional) are listed for the generators of the little co-group $\mathcal{G}^{\Delta}$.

| | Irreducible representations | | | |
|---|---|---|---|---|
| Generators | Δ1 | Δ2 | Δ3 | Δ4 |
| $2_y$ | 1 | 1 | −1 | −1 |
| $m_z$ | 1 | −1 | 1 | −1 |

$\boldsymbol{D}^{\Gamma,\tau}$ subduced to $2mm$, fulfil the condition equation (7), and these irreducible representations are Γ1 and Γ4.

Due to the non-symmorphic character of *Pnma*, the factors $\exp(-i\mathbf{H}\cdot\boldsymbol{w}^{\mathbf{q}})$ may take values ±1 depending on the Brillouin zone vector and the non-primitive translation $\boldsymbol{w}^{\mathbf{q}} = (w_1^{\mathbf{q}}, w_2^{\mathbf{q}}, w_3^{\mathbf{q}})$. For example, in the case of **H**(0, 0, $l$) and a little-group element $(\boldsymbol{W}^{\mathbf{q}}, \boldsymbol{w}^{\mathbf{q}})$, with $w_3^{\mathbf{q}} = \frac{1}{2}$, this factor is equal to 1 for $l = 2n$, and −1 for $l = 2n + 1$. As a result one gets a different set of selection rules depending on the parity of $l$. For Brillouin zones centred at non-extinct Bragg reflections, the selection rules coincide with those of *Pmmm*. The specific selection rules for *Pnma* are at Brillouin zones whose centres are extinct Bragg reflections.

### 6.2. Example 2

As a second example, let us consider the case of a crystal of *Cmmm* symmetry, and let us suppose we are specially interested to investigate phonons with wavevector **q** = (1, 0, 0),[2] *i.e.* phonons at the point **Y** of the Brillouin zone (*cf.* Cracknell *et al.*, 1979). The irreducible representations for this wavevector are listed in Table 1. The list of selection rules for these phonons, as obtained by the program *NEUTRON*, are listed in Table 3. The wavevector **q** = (1, 0, 0) is equivalent to the vector **q** = (0, 1, 0) by a reciprocal-lattice vector. It is illustrative to see what is the output of *NEUTRON* if we choose as a representative for the **Y** point, this alternative vector (Table 3). The selections rules are expressed in a different form, as the reference Brillouin zone centre for a given scattering vector **Q** is changed, but they are fully equivalent. *NEUTRON* can deal with any representative of the phonon wavevectors, *i.e.* the **q** vector coefficients are not restricted to any representation domain and/or Brillouin zone.

[2] The coordinates are referred to the conventional (dual) basis of the reciprocal space; $(\frac{1}{2}, \frac{1}{2}, 0)$ would be the coordinates with respect to a primitive basis of the reciprocal space.

**Table 5**
Selection rules for **Δ** phonons, space group *Cmmm*.

The symmetry types (irreducible representations) of phonons which can be INS active (allowed) are listed for a representative **H**($h$, $k$, $l$) of a Brillouin zone class ($n$ integer). The groups $\overline{\mathcal{G}}^{\mathbf{Q}}$ are given as oriented site-symmetry symbols. For the irreducible-representation labels, see Table 4.

| | **Δ** phonons, $\overline{\mathcal{G}}^{\mathbf{Y}} = mmm$, $\mathbf{Q} = \mathbf{H} - \mathbf{\Delta} = (h, k - \alpha, l)$ | |
|---|---|---|
| Brillouin zone | $\overline{\mathcal{G}}^{\mathbf{Q}}$ | INS-active types of phonons |
| **H**(0, $k$, 0) $k = 2n$ | $m2m$ | Δ1 |
| **H**($h$, $k$, 0) $h + k = 2n$ | $..m$ | Δ1, Δ3 |
| **H**(0, $k$, $l$) $k = 2n$ | $m..$ | Δ1, Δ4 |

An essential point when measuring phonon energies by inelastic neutron scattering with a three-axis spectrometer is to decide the scattering plane on which the measurements are going to be performed. In an orthorhombic system, the choice is usually reduced to either the ($hk$0), the ($h$0$l$) or the (0$kl$) planes. As an application of Table 3, let us imagine that we are specifically interested to detect and measure phonons transforming according to a particular irreducible representation, say Y7, with **Y** = (1, 0, 0), the reason being for instance that the softening of a mode of this symmetry is the signature of a specific phase transition. According to Table 3, the only favourable choice of scattering plane is the plane (0$kl$). The Y7 phonons are visible at scattering vectors **Q** = (0$kl$) with $l$ not zero and $k$ odd, *i.e.* at *C*-centring extinct Bragg vectors [except those at the axis (0$k$0)]. At these (0$kl$) points, irreducible representations Y6, Y4 and Y1 are also active. On the other hand, at points (0$k$0) with $k$ odd, both Y7 and Y4 phonons become extinct. Therefore a comparison of the measurements at these two types of points will allow one to identify those phonons having either Y7 or Y4 symmetry. However, to identify univocally the Y7 phonons, a third type of scattering vectors on a different scattering plane would have to be investigated, namely those of type ($h$0$l$) with $h$ odd, where the Y4 phonons are active, while the Y7 phonons are not.

A second important practical point is to know whether the phonon branches associated with the Y7 phonons will also be visible along specific symmetry lines. For instance, the line **Δ** of wavevectors **q** = (0, $\alpha$, 0), with $0 < \alpha < 1$, connects points **Γ** and **Y**, and has $m2m$ as little co-group. If active, phonons along this line would be measurable on the plane (0$kl$). The selection rules obtained for this line are listed in Table 5. By compatibility, the phonon branches along the **Δ** line, and having symmetry Y7 at the **Y** point, have symmetry Δ4 (see Table 4). One can see that the scattering plane (0$kl$), with scattering vectors **Q** = (0, $k - \alpha$, $l$), is again the only favourable choice for observing these branches.

## 7. Conclusions

We have developed the computer program *NEUTRON* for the determination of phonon selection rules in INS and TDS experiments. The applied algorithm is based on a recently proven theorem that demonstrates the existence of symmetry-based (structure-independent) selection rules for the phonon activity in INS experiments. The systematic absences depend on the phonon mode symmetry and the Brillouin zone where the measurement takes place. The computer program forms part of the Bilbao Crystallographic server (http://

www.cryst.ehu.es) and it can be used *via* the Internet from any computer with a Web browser.

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