Phonon Symmetry Selection Rules for Inelastic Neutron Scattering

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A theorem is proven demonstrating the existence of phonon symmetry selection rules, independent of particular structural features, for coherent inelastic neutron scattering by crystals. The resulting systematic absences depend only on the mode symmetry and the Brillouin zone where the measurement takes place. Several examples show their power for identifying the symmetries of measured phonon branches. Despite their importance and simplicity, these structure-independent extinction rules, based only on symmetry arguments, have, to our knowledge, never been formulated and are not currently considered in the analysis of phonon scattering data. [S0031-9007(98)06876-8]

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The determination of crystal phonon frequencies through experiments of coherent inelastic neutron scattering (INS) is now a rather standard technique in solid state physics. Conservation of crystalline momentum implies that one-phonon emission (absorption) processes for a particular mode j, of wave vector $\mathbf{q}(-\mathbf{q})$, can be observed only at scattering vectors $\mathbf{Q}$, such that $\mathbf{Q} + \mathbf{q}$ is a reciprocal lattice vector. Hence, repeated measurements at different $\mathbf{Q}$ values, allow one, in principle, to determine the phonon branches $\omega_j(\mathbf{q})$ [1]. However, a proper interpretation of the results and/or an unambiguous comparison with theoretical predictions requires, in many cases, additional information on the symmetry of each mode, i.e., the small irreducible representation (irrep) describing its transformation properties [2]. Usually, only partial symmetry assignments are done by comparison with other spectroscopic results as Raman or infrared frequencies, or making use of the well-defined symmetry properties of acoustic branches. Sometimes, calculations using more or less complex lattice dynamical models are also performed and the irrep labels of the measured phonon branches are identified by similarity with the calculated ones. On the other hand, some authors have been aware of the existence of some kind of extinction rules in INS experiments, which were explained using various arguments related with specific structural or symmetry features of the material under study [3]. In the few cases where general rules have been discussed, they have been considered in a complex framework that depends not only on symmetry arguments, but also on the actual structure (i.e., on the atomic positions) [4,5]. Indeed, it is a quite widespread belief that INS experiments do not obey any particular systematic symmetry extinction rules except for the wave vector relation mentioned above and the obvious ones coming from the transverse or longitudinal character of their polarization vectors (see, for instance, Ref. [6]). To our knowledge, a rule regarding systematic phonon absences in INS spectra, based only on the space group of the material, the symmetry of the phonon, and the scattering vector $\mathbf{Q}$, has never been formulated and is not currently being used in the analysis or preparation of INS experiments. The purpose of this Letter is to demonstrate that, in fact, such a general rule exists and can be extremely useful when systematically applied.

The scattered neutron intensity due to a mode j, of wave vector $\mathbf{q}$, and polarization vector $\mathbf{e}(\mu \,|\, \mathbf{q}, j)$, measured at a particular scattering vector $\mathbf{Q}$, such that $\mathbf{Q} + \mathbf{q}$ is a reciprocal lattice vector, is proportional to $|F_j(\mathbf{Q})|^2$, where $F_j(\mathbf{Q})$ is the one-phonon dynamical structure factor for INS, and is given by [1,6]

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

where the index μ labels the atoms (nuclei) in a primitive unit cell, m_μ is the mass of atom μ, b_μ is its coherent scattering length, $W_\mu(\mathbf{Q})$ is the exponent of the corresponding Debye-Waller factor. In the case of n degenerate modes transforming according to a n-dimensional (small) irrep $D^{\mathbf{q},\tau}$, the scattered intensity is proportional to $\sum_{j=1}^{n} |F_j(\mathbf{Q})|^2$.

According to well-known expressions from the group-theoretical formalism of lattice dynamics, the action of any crystal symmetry operation $\{\mathbf{R} \,|\, \mathbf{t}\}$ belonging to the space group of the wave vector $\mathbf{q}$, $G_\mathbf{q}$, on a mode of polarization vector $\mathbf{e}(\mu \,|\, \mathbf{q}, j)$, transforms the mode into a new one with polarization vector $\mathrm{P}\{\mathbf{R} \,|\, \mathbf{t}\}\mathbf{e}(\mu \,|\, \mathbf{q}, j)$, which is given by [2,7]

$$P\{\mathbf{R} \,|\, \mathbf{t}\}\mathbf{e}(\mu \,|\, \mathbf{q}, j) = \mathbf{R}\,\mathbf{e}(\nu \,|\, \mathbf{q}, j) \exp(-i\mathbf{R}\mathbf{q} \cdot \mathbf{t}) \times \exp[i(\mathbf{R}\mathbf{q} - \mathbf{q}) \cdot \mathbf{r}_\mu], \quad (2)$$

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where atom v is the symmetry equivalent to μ by operation $\{\mathbf{R} \mid \mathbf{t}\}$. On the other hand, this action can also be considered as a transformation described by the small irrep $D^{\mathbf{q},\tau}$, and this implies

$$\mathrm{P}\{\mathbf{R} \mid \mathbf{t}\}\mathbf{e}(\mu \mid \mathbf{q}, j) = \sum_{i=1,n} D^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})_{ij}\mathbf{e}(\mu \mid \mathbf{q}, i), \quad (3)$$

where the label $i = 1, \ldots, n$ runs over the n degenerate modes transforming according to $D^{\mathbf{q},\tau}$ and $D^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})_{ij}$ represent the corresponding matrix coefficients for this irrep. Combining both Eqs. (2) and (3) and taking into account the rotational symmetry between the Debye-Waller terms, it is straightforward to derive that the dynamical structure factor given by Eq. (1), and corresponding to these n degenerate modes, satisfies

$$F_i(\mathbf{R}\mathbf{Q}) = \sum_{j=1,n} D^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})^*_{ij} \exp(i\mathbf{R}\mathbf{Q} \cdot \mathbf{t})F_j(\mathbf{Q}). \quad (4)$$

For a general $\mathbf{Q}$, this equation implies the trivial result that $\sum_{j=1}^{n} |F_j(\mathbf{Q})|^2 = \sum_{j=1}^{n} |F_j(\mathbf{R}\mathbf{Q})|^2$, i.e., the scattered intensities are equivalent for scattering vectors rotated by $\mathbf{R}$. However, for any $\mathbf{R}$ belonging to the (strict) point group [8] of $\mathbf{Q}$, $\mathrm{P}_{\mathbf{Q}}^{(s)}$ (i.e., for any $\mathbf{R}$ such that $\mathbf{R}\mathbf{Q} = \mathbf{Q}$) Eq. (4) reduces to

$$F_i(\mathbf{Q}) = \sum_{j=1,n} T_{\mathbf{Q},\tau}(\mathbf{R})_{ij}F_j(\mathbf{Q}), \quad (5)$$

where $T_{\mathbf{Q},\tau}$ is a representation of $P_{\mathbf{Q}}^{(s)}$ which is related to the small irrep $D^{\mathbf{q},\tau}$ in the form:

$$T_{\mathbf{Q},\tau}(\mathbf{R}) = D^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})^* \exp(i\mathbf{Q} \cdot \mathbf{t}). \quad (6)$$

According to Eq. (5), the set of dynamical structure factors $\{F_j(\mathbf{Q})\}$ is fully invariant for all transformations $T_{\mathbf{Q},\tau}(\mathbf{R})$, with $\mathbf{R}$ belonging to $P_{\mathbf{Q}}^{(s)}$. This can happen only for a set of nonzero values $F_j(\mathbf{Q})$, if the representation $T_{\mathbf{Q},\tau}$ of $P_{\mathbf{Q}}^{(s)}$ contains the identity irrep. Hence, we can state the following theorem: *All phonon modes of wave vector $\boldsymbol{q}$ and symmetry given by the small irrep $D^{\mathbf{q},\tau}$ will be INS inactive at a scattering wave vector $\boldsymbol{Q}$ (even though $\boldsymbol{Q} + \boldsymbol{q}$ is a reciprocal lattice vector), if the representation of $P_{\boldsymbol{Q}}^{(s)}$ constructed as described in Eq. (6) does not contain the identity irrep at least once.*

Using the well-known "magic" formula from group theory [2], this can be reformulated: *All phonon modes of wave vector $\boldsymbol{q}$ and symmetry given by the small irrep $D^{\mathbf{q},\tau}$ will be INS inactive at a scattering wave vector $\boldsymbol{Q}$ (even though $\boldsymbol{Q} + \boldsymbol{q}$ is a reciprocal lattice vector), if*

$$\sum_{\mathbf{R} \in P_{\mathbf{Q}}^{(s)}} \chi^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})^* \exp(i\mathbf{Q} \cdot \mathbf{t}) = 0, \quad (7)$$

where $\chi^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})$ is the character of the operation $\{\mathbf{R} \mid \mathbf{t}\}$ for the small irrep $D^{\mathbf{q},\tau}$.

The determination for a given $\mathbf{q}$ vector of all possible selection rules depending on the type of $\mathbf{Q}$ vector requires a previous classification of the latter into subsets according to their $P_{\mathbf{Q}}^{(s)}$ (i.e., a classification of the $\mathbf{Q}$ vectors into different orbits with respect to the point group of $\mathbf{q}$, $P_{\mathbf{q}}$). As $\mathbf{Q} = \mathbf{H} - \mathbf{q}$, where $\mathbf{H}$ is a reciprocal lattice vector, an operation $\mathbf{R}_i$ belonging to $P_{\mathbf{q}}$ will also belong to $P_{\mathbf{Q}}^{(s)}$ if $\mathbf{R}_i\mathbf{H} - \mathbf{K}_i = \mathbf{H}$, where $\mathbf{K}_i$ is the reciprocal lattice vector satisfying $\mathbf{K}_i = \mathbf{R}_i\mathbf{q} - \mathbf{q}$. In general, two situations can be distinguished.

(i) *The wave vector $\boldsymbol{q}$ is not on the Brillouin zone boundaries.*—In this case, $\mathbf{K}_i = 0$ for all operations in $P_{\mathbf{q}}$. Then $P_{\mathbf{Q}}^{(s)} = P_{\mathbf{H}}^{(s)} \cap P_{\mathbf{q}}$. $P_{\mathbf{Q}}^{(s)}$ is the intersection of the point group of $G_{\mathbf{q}}$ and the (strict) point group of the reciprocal lattice vector $\mathbf{H}$ associated to the Brillouin zone where the measurement takes place. The character $\chi^{\mathbf{q},\tau}(\{\mathbf{R} \mid \mathbf{t}\})$ can be expressed, in this case, as $\chi^{\tau}(\mathbf{R}) \exp(-i\mathbf{q} \cdot \mathbf{t})$, with $\chi^{\tau}(\mathbf{R})$ being the character of an irrep τ of the point group $P_{\mathbf{q}}$. Therefore, Eq. (7) reduces to

$$\sum_{\mathbf{R} \in P_{\mathbf{Q}}^{(s)}} \chi^{\tau}(\mathbf{R})^* \exp(i\mathbf{H} \cdot \mathbf{t}) = 0. \quad (8)$$

We can interpret Eq. (8) as a check that the identity irrep is not contained in the Kronecker product of the two irreps, τ and $\exp(i\mathbf{H} \cdot \mathbf{t})$, of $P_{\mathbf{q}}$ and $P_{\mathbf{H}}^{(s)}$, respectively, when reduced to their common subgroup $P_{\mathbf{Q}}^{(s)}$. For symmorphic space groups, $\exp(i\mathbf{H} \cdot \mathbf{t}) = 1$ for any $\mathbf{H}$, and the selection rule becomes a simple check of whether the representation subduced in $P_{\mathbf{Q}}^{(s)}$ by the irrep τ contains the identity representation or not. The resulting extinctions are also valid for nonsymmorphic groups, if the vector $\mathbf{H}$ is such that $\exp(i\mathbf{H} \cdot \mathbf{t}) = 1$ for all elements $\{\mathbf{R} \mid \mathbf{t}\}$ with $\mathbf{R}$ belonging to the point group $P_{\mathbf{Q}}^{(s)}$. The reciprocal lattice vectors corresponding to nonextinct Bragg diffraction reflections fulfill this condition. Hence, it can be generally stated that: The selection rules for phonons of a nonsymmorphic space group coincide with those of the corresponding symmorphic group, if the Brillouin zone of the measurement is centered in a nonforbidden Bragg reflection. Conversely, in Brillouin zones centered on extinct Bragg reflections, new phonon extinction rules exist that depend on the nonprimitive translational part of the symmetry operations.

(ii) *The wave vector $\boldsymbol{q}$ is on the Brillouin zone boundary.*—In this second case, as $\mathbf{K}_i$ may be nonzero for some operations of $P_{\mathbf{q}}$, $P_{\mathbf{Q}}^{(s)}$ may contain operations not belonging to $P_{\mathbf{H}}^{(s)}$. Equation (8) can still be taken as valid, but then, in the most general case of a nonsymmorphic space group, the characters $\chi^{\tau}(\mathbf{R})$ in the equation should be reinterpreted as those of a multiplier (weighted) irrep of $P_{\mathbf{q}}$ [2]. However, one can always avoid the use of multiplier irreps and use directly Eq. (7), the small irreps of $G_{\mathbf{q}}$ being determined through a direct algorithm (see, for instance, Ref. [9]).

As examples, we discuss now the resulting selection rules for modes with $\mathbf{q} = 0$ (point Γ), $\mathbf{q} = (\alpha, 0, 0)$

(line Σ or Δ), and $\mathbf{q} = (\frac{1}{2}, 0, 0)$ (point X) for some space groups. The selection rules are indicated in the following manner: The Brillouin zone centers $\mathbf{H}$, where some extinction exists for phonons observed at $\mathbf{Q} = \mathbf{H} - \mathbf{q}$, are listed and in each case the irreps of the phonons which are "active" and will appear in the INS experiment are given. The irrep labels are those from Ref. [10].

(1) *Space group Pmm2.*—Point Γ: The sets of Brillouin zone vectors $\mathbf{H}(=\mathbf{Q})$ with nontrivial symmetry are: $(0,\ 0,\ l)$ $[mm2]$; $(0,\ k,\ l)$ $[m11]$; and $(h,\ 0,\ l)$ $[1m1]$, where we have indicated in brackets the corresponding point group $P_{\mathbf{Q}}^{(s)}$. There are four possible irreps of $P_{\mathbf{q}}(=mm2)$: Γ_1 (fully symmetric), Γ_2 (antisymmetric for m_x and m_y), Γ_3 (antisymmetric for m_y and 2_z), and Γ_4 (antisymmetric for m_x and 2_z). Applying Eq. (8) or just by simple inspection, taking into account that $\exp(i\mathbf{H} \cdot \mathbf{t}) = 1$ in all cases, the following selection rules are obtained: $(0,\ 0,\ l)-\Gamma_1$; $(0,\ k,\ l)$ $k \neq 0-\Gamma_1,\ \Gamma_3$; and $(h,\ 0,\ l)$ $h \neq 0-\Gamma_1,\ \Gamma_4$. One can see that Γ_2 is silent except at a general Brillouin zone, and, in principle, it is sufficient to make a measurement at three different Brillouin zones to identify the symmetry of all measured Γ phonons. Line Σ: $P_{\mathbf{q}} = 1m1$, with two irreps: Σ_1 (fully symmetric) and Σ_2 (antisymmetric for m_y). $P_{\mathbf{Q}}^{(s)}$ does not coincide now with $P_{\mathbf{H}}^{(s)}$, but is a subgroup. The application of the general equation is again straightforward yielding $(h,\ 0,\ l)-\Gamma_1$ $[1m1]$, where we indicate in brackets, the corresponding point group $P_{\mathbf{Q}}^{(s)}$. For $(0,\ k,\ l)$, no extinction exists as $P_{\mathbf{Q}}^{(s)}$ reduces to the group identity. Point X: $P_{\mathbf{q}} = mm2$, with four irreps X_i, $i = 1, \ldots, 4$, whose labeling scheme follows the one mentioned above for the point Γ. However, the possible symmetries of the scattering vector $\mathbf{Q}$ are reduced to those already discussed for line Σ. Hence, a single selection rule exists: $(h,\ 0,\ l)-X_1,\ X_4$ $[1m1]$. This last rule could be expected by continuity, since these two X irreps are those compatible with Σ_1, which is the only active irrep at line Σ for these Brillouin zones (see above).

(2) *Space group Pnn2.*—Point Γ: The discussion above for $Pmm2$ concerning the subsets of different Brillouin zone centers and the possible irreps of the modes is also valid for a nonsymmorphic space group. However, now $\exp(i\mathbf{H} \cdot \mathbf{t})$ is not trivial. As the values of the nonprimitive translation are $(\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2})$, $(\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2})$, $(0,\ 0,\ 0)$ for m_x, m_y, and 2_z, respectively, it is straightforward to obtain the corresponding values of $\exp(i\mathbf{H} \cdot \mathbf{t})$ for different types of $\mathbf{H}$ and apply Eq. (8):

$$(0,\ 0,\ l)\ l\ \text{even}-\Gamma_1;\ l\ \text{odd}-\Gamma_2\,,$$

$$(0,\ k,\ l)\ k \neq 0,\ k + l\ \text{even}-\Gamma_1, \Gamma_3;\ k + l\ \text{odd}-\Gamma_2, \Gamma_4\,,$$

$$(h,\ 0,\ l)\ h \neq 0,\ h + l\ \text{even}-\Gamma_1, \Gamma_4;\ h + l\ \text{odd}-\Gamma_2, \Gamma_3\,.$$

As expected, equivalent selection rules as those for $Pmm2$ are obtained at Brillouin zones centered at nonextinct Bragg reflections (even parities). Line Σ: The same considerations are valid and a different selection rule appears only at Brillouin zones corresponding to extinct Bragg reflections: $(h,\ 0,\ l)$ $h \neq 0$, $h + l$ even–Σ_1; $h + l$ odd–Σ_2. Point X: No selection rule exists for this point.

(3) *Space group Pnma.*—The set of possible symmetry types of vectors $\mathbf{H}$ for the Brillouin zone is now larger: $(0, 0, l)$ $[mm2]$; $(0, k, 0)$ $[m2m]$; $(h, 0, 0)$ $[2mm]$; $(0, k, l)$ $[m11]$; $(h, 0, l)$ $[1m1]$; and $(h, k, 0)$ $[11m]$. The line Σ has $2mm$ symmetry and the point X has again the full symmetry mmm. Let us consider first the resulting selection rules for the point Γ and line Σ. Point Γ:

$$(0, 0,\ l)\ l \neq 0,\ l\ \text{even}-\Gamma_1^+, \Gamma_2^-;\ l\ \text{odd}-\Gamma_4^+, \Gamma_3^-\,,$$

$$(0,\ k,\ 0)\ k \neq 0,\ k\ \text{even}-\Gamma_1^+, \Gamma_4^-;\ k\ \text{odd}-\Gamma_2^+, \Gamma_3^-\,,$$

$$(h,\ 0,\ 0)\ h \neq 0,\ h\ \text{even}-\Gamma_1^+, \Gamma_3^-;\ h\ \text{odd}-\Gamma_4^+, \Gamma_2^-\,,$$

$$(0,\ k,\ l)\ k, l \neq 0,\ k + l\ \text{even}-\Gamma_1^+, \Gamma_3^+, \Gamma_2^-, \Gamma_4^-;\ k + l\ \text{odd}-\Gamma_2^+, \Gamma_4^+, \Gamma_1^-, \Gamma_3^-\,,$$

$$(h,\ 0,\ l)\ h, l \neq 0-\Gamma_1^+, \Gamma_4^+, \Gamma_2^-, \Gamma_3^-\,,$$

$$(h,\ k,\ 0)\ h, k \neq 0,\ h\ \text{even}-\Gamma_1^+, \Gamma_2^+, \Gamma_3^-, \Gamma_4^-;\ h\ \text{odd}-\Gamma_3^+, \Gamma_4^+, \Gamma_1^-, \Gamma_2^-\,.$$

Line Σ:

$$(h, 0, 0)\ h\ \text{even}-\Sigma_1;\ h = \text{odd}-\Sigma_3\,,$$

$$(h,\ 0,\ l)\ l \neq 0-\Sigma_1, \Sigma_3\,,$$

$$(h,\ k,\ 0)\ k \neq 0,\ h\ \text{even}-\Sigma_1, \Sigma_4;\ h\ \text{odd}-\Sigma_2, \Sigma_3\,.$$

The extinction rules at Brillouin zones whose centers are extinct Bragg reflections due to nonsymmorphic operations (odd parities) are specific for the space group $Pnma$. The rest are common with the space group $Pmmm$. Note that for some Brillouin zones the selection rules may be as restrictive as Raman or infrared spectroscopy. It is clear that by combining measurements at different types of Brillouin zones all symmetry labels for the measured phonons can be identified. In principle, both for the point Γ and the line Σ, it would be sufficient to perform INS measurements at three different Brillouin zones. Point X: There are only two bidimensional small irreps to be considered [10] and again, as the points X lie on the border between Brillouin zones with alternative selection rules for the line Σ, the few remaining selection rules are those to be expected from the compatibility relations $X_1 = \Sigma_1 + \Sigma_3$ and $X_2 = \Sigma_2 + \Sigma_4$: $(h,\ 0,\ l)$ $l \neq 0-\mathrm{X}_1$.

(4) *Space Group $Pn\bar{3}m$.*—Point Γ:

$$(h,\ 0,\ 0)\ h \neq 0,\ h\ \text{even}-\Gamma_1^+, \Gamma_3^+, \Gamma_4^-;$$
$$h\ \text{odd}-\Gamma_2^-, \Gamma_3^-, \Gamma_5^+,$$
$$(h,\ h,\ h)\ h \neq 0-\Gamma_1^+, \Gamma_5^+, \Gamma_2^-, \Gamma_4^-,$$
$$(0,\ k,\ k)\ k \neq 0-\Gamma_1^+, \Gamma_3^+, \Gamma_5^+, \Gamma_4^-, \Gamma_5^-,$$
$$(0,\ k,\ l)\ k,\ l \neq 0,$$
$$k + l\ \text{even}-\Gamma_1^+, \Gamma_2^+, \Gamma_3^+, \Gamma_4^+, \Gamma_5^+, \Gamma_4^-, \Gamma_5^-,$$
$$k + l\ \text{odd}-\Gamma_4^+, \Gamma_5^+, \Gamma_1^-, \Gamma_2^-, \Gamma_3^-, \Gamma_4^-, \Gamma_5^-,$$
$$(h,\ k,\ k)\ h,k \neq 0-\Gamma_1^+, \Gamma_3^+, \Gamma_4^+, \Gamma_5^+, \Gamma_2^-, \Gamma_3^-, \Gamma_4^-, \Gamma_5^-.$$

Line Δ ($\mathbf{q} = (\alpha,\ 0,\ 0)$):

$$(h,\ 0,\ 0)\ h\ \text{even}-\Delta_1;\ h = \text{odd}-\Delta_3,$$
$$(h,\ 0,\ l), (h,\ k,\ 0)\ l(k) \neq 0\ h + l(k)\ \text{even}-\Delta_1, \Delta_2, \Delta_5$$
$$h + l(k)\ \text{odd}-\Delta_3, \Delta_4, \Delta_5,$$
$$(h,\ k,\ k), (h,\ k,\ -k)\ k \neq 0-\Delta_1, \Delta_3, \Delta_5.$$

Point X:

$$(h,\ 0,\ 0)\ X_1,$$
$$(h,\ k,\ k), (h,\ k,\ -k)\ k \neq 0-X_1, X_3, X_4.$$

For the point Γ, only the selection rules for a single representative Brillouin zone within each set of symmetry equivalent ones is listed. For instance, $(0,\ k,\ k)$ is indicated as representative for the set $(0,\ k,\ \pm k)$, $(h,\ \pm h,\ 0)$, and $(h,\ 0,\ \pm h)$, which have equivalent extinction rules with identical allowed irreps.

It is interesting to compare the results for $Pn\bar{3}m$ with the selection rules determined by Elliot and Thorpe [4] for Cu_2O. One can clearly see the difference between the two approaches. Cuprite has only a few atoms in the unit cell at high-symmetry positions. Hence, similarly as for diffraction, extra extinction rules exist in addition to those resulting from space group symmetry. These two very different kinds of extinction rules are not distinguished in Ref. [4], and all of them are derived by making use of the specific atomic positions of the cuprite structure. For point Γ, the extinction rules in cuprite (see Table 4 in Ref. [4]) are much more restrictive than those listed above, being in each case a subset. Only in the case of Brillouin zones of type $(h,\ 0,\ 0)$, the three allowed irreps for the general case are also active in cuprite. For the line Δ, however, nearly all selection rules have their origin in the general space group symmetry, the specific structure introduces only the additional absence of irrep Δ_3 at Brillouin zones of type $(h,\ k,\ k)$ (see Table 5 in Ref. [4]). Obviously, the extinction rules exclusively based on the space group symmetry, as derived here, are those to be expected in a complex structure, where the atomic positions are not reduced to a few high-symmetry positions.

It is also important to note that the general selection rules formulated above include the trivial extinctions of transversal and longitudinal modes resulting from the factor $(\mathbf{Q} \cdot \mathbf{e})$ in the structure factor formula.

Summarizing, a general method is proposed for deriving phonon extinction rules in INS experiments. The formulation is quite simple and demonstrates that very restrictive phonon absences can happen for certain types of scattering wave vectors, independently of the specific atomic positions in the crystal structure. The derived selection rules can be used to identify the symmetries of the measured phonons or to choose adequate scattering vectors to prevent the overlapping of phonon responses. Their systematic use will surely help to optimize the preparation of INS experiments and the analysis of the resulting data.

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