Continuity of Phonon Spectra for Diamond and Hexagonal Close Packed Structures

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Band representations of space groups are used for showing that crystals with diamond or hexagonal close packed structures have phonon spectra that extend from zero to some maximal frequency without a gap in between. This gapless feature follows from the vectorial nature of lattice vibrations, from the continuity that is introduced by band representations, and from the symmetry of Bloch functions for nonsymmorphic space groups. Some other space groups having two identical atoms in a unit cell and leading to the same continuity feature for their phonon spectrum are listed.

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From the very beginning of applying group theory to Bloch electrons much emphasis was put on continuity [1]. This was done via the introduction of compatibility relations between different symmetry points in the Brillouin zone. It was soon realized that these relations apply equally well to phonons [2]. Through the years the compatibility relations have turned into an indivisible part of the symmetry labeling for electrons and phonons in crystalline solids [3]. An additional step in the understanding of continuity in the band structure was made by establishing a symmetry connection between localized and extended functions [4–6]. More recently, the continuity of energy spectra was formulated by means of band representations [7] and the introduction of continuity chords [8]. Unlike an irreducible representation which labels the symmetry of a Bloch function at a given point in the Brillouin zone, a band representation labels the symmetry of a whole band as a continuous entity via the assignment of a symmetry label to its Wannier function. A band representation with its continuity chord contains the full information of all compatibility relations for the given band. A classification of band representations is presented in Ref. [9]. Some applications of band representations to various excitations in solids are given in a recent book on the subject [10]. The symmetry classification of Ref. [9] applies equally to electrons and phonons. However, since band representations are induced from local symmetry groups [4–8], some restrictions apply to phonons which are a consequence of the vectorial nature of lattice vibrations. One restriction has to do with the fact that, when inducing a band representation, one has to start with a vector representation of the local symmetry group. The other restriction follows from the number of frequency branches for a given solid which equals $3n$, where n is the number of atoms in a unit cell. These two restrictions reduce considerably the number of band representations for phonons. Thus for a solid with one atom in a unit cell a single vectorial band representation contains a complete symmetry description of its three-branch phonon spectrum. Bearing in mind that all three branches are acoustic with vanishing frequency ω for zero quasimomentum, $\mathbf{k} = 0$, one deduces that crystals with one atom in a unit cell have a frequency spectrum extending continuously from zero to some maximal frequency $\omega_{\max}$. When looking at phonon dispersion relations of crystals having two identical atoms in a unit cell with diamond (Ge, Si, etc.) or hexagonal close packed (Be, Mg, etc.) structures, one observes a similar striking feature: the six phonon branches extend continuously in frequency from zero to some maximal frequency $\omega_{\max}$ without a gap in the spectrum [3,11,12]. In following numerous other materials with diamond or hexagonal close packed structures [13], it turns out that this continuity feature in their phonon spectrum is a rule without exceptions to it. One therefore expects that a general explanation should exist for this striking continuity rule.

In this Letter band representations are used for showing that crystals with diamond or hexagonal close packed structures have necessarily gapless phonon frequency spectra. It turns out that this continuous nature of the spectrum is mainly a consequence of the fact that the phonon band representations for these crystals are induced from a single vectorial representation of the corresponding local symmetry group. It is pointed out that many other crystals with two identical atoms in a unit cell possess this continuity feature in their phonon spectrum. In contrast, when the two atoms in the unit cell are different, the band representation for phonons is no longer induced from a simple vectorial representation and a gap appears, in general, in the frequency spectrum. Examples are spectra of the CsCl-type crystals [11–13].

For building a band representation [7,14] one starts with a symmetry center $\mathbf{q}$ (called the Wyckoff position [15]) and a little group G_q which leaves this center unchanged. For phonons one defines a set of three ($j = 1, 2, 3$) vector

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functions $\mathbf{v}_j(\mathbf{r})$. The vector function $\mathbf{v}_j(\mathbf{r})$, for a given j, is defined at all equilibrium ion positions $\mathbf{r}$, and represents the most general displacement of the ion at $\mathbf{r}$ consistent with $\mathbf{v}_j(\mathbf{r})$ transforming as the jth basis vector of the (three-dimensional) vector representation of G_q, i.e.,

$$g\mathbf{v}_j(\mathbf{r}) = \sum_{j'} D_{j'j}(g)\mathbf{v}_{j'}(\mathbf{r}), \tag{1}$$

where g is an element of G_q. The band representation $D^{(b)}$ is then the representation [16] of the full space group G induced from the representation D of G_q. In terms of the basis vectors v_j of Eq. (1) the band representation is built in the following way. One decomposes G into left cosets with respect to the group G_q,

$$G = TG_q + T(\alpha_2 \mid \mathbf{t}(\alpha_2))G_q + \cdots + T(\alpha_s \mid \mathbf{t}(\alpha_s))G_q, \tag{2}$$

where T is the translation group, s is the multiplicity of the Wyckoff position, and $(\alpha \mid \mathbf{t}(\alpha))$ are space group elements [α is a point group element and $\mathbf{t}(\alpha)$ is a fractional translation]. For obtaining the band representation one has to apply all the elements of G in Eq. (2) to the vector function $\mathbf{v}_j(\mathbf{r})$ in Eq. (1). This can be done in two steps. By applying the elements $(\alpha_f \mid \mathbf{t}(\alpha_f))$ with $f > 1$ to $\mathbf{v}_j(\mathbf{r})$ [$(\alpha_1 \mid \mathbf{t}(\alpha_1))$ *is the unit element*] we have

$$(\alpha_f \mid \mathbf{t}(\alpha_f))\mathbf{v}_j(\mathbf{r}), \qquad f = 2, \ldots, s. \tag{3}$$

This action leads to $s - 1$ new vectors that are assigned to different sites in the unit cell. Then we apply all the Bravais lattice translations $\mathbf{R}_n$ to these s vectors. Applying translations is nothing else but shifting the s vectors in Eq. (3) to new sites on the crystal lattice. One ends up with s infinite sets of vectors that form the basis for the band representation $D^{(b)}$. It should be pointed out that s is the number of vectorial orbitals or the number of Wyckoff positions in the star [7]. The above built band representation corresponds to a phonon spectrum with $3s$ branches (three branches for each vector). When there is one atom in the unit cell, $G = G_qT$ in Eq. (2) is the full space group and the above induction process will lead to a three-branch phonon spectrum. For crystals with two atoms in a unit cell (diamond and hexagonal close packed structures) we get a six-branch spectrum. We point out that the vectors in Eq. (3) (together with the translated ones) are by no means the actual vibration vectors for the atoms in the crystal. The latter, however, can be obtained as linear combinations of the former. In the general case of s identical atoms in a unit cell the induction process of Eqs. (1)–(3) leads to some continuous mixing of all the $3s$ branches, and it would be improbable to expect that some of them would split off as a group and form a gap in the phonon spectrum. There is no proof for this general statement. The claim of the continuous mixing of the $3s$ branches is connected to the concept of elementary band representations [9]. The latter are band representations that cannot be written as a direct sum of band representations. The word improbable is used here to point out that such a splitting cannot appear without the lowering of the symmetry. However, in what follows, we are going to show that for diamond and hexagonal close packed structures the six-branch phonon spectrum is necessarily a continuum without gaps in it.

We start with crystals of diamond structure. Their space group is O_h^7 $(Fd\bar{3}m)$ and according to Ref. [15] there are two Wyckoff positions that accommodate two atoms in a unit cell. These are the positions a and b as shown in Table I. Both have the full point symmetry of a tetrahedron T_d. Let us first concentrate on the Wyckoff position a (see Ref. [3]). The space group O_h^7 decomposition of Eq. (2) for this position is (a is also the lattice constant)

$$O_h^7 = TT_d(a) + T\left(I \;\middle|\; \frac{a}{4}\frac{a}{4}\frac{a}{4}\right)T_d(a), \tag{4}$$

where $(I \mid \frac{a}{4}\frac{a}{4}\frac{a}{4})$ is the inversion I accompanied by the fractional translation $(\frac{a}{4}\frac{a}{4}\frac{a}{4})$ and $T_d(a)$ is the set of point group elements of the site $(0,0,0)$. Following the construction scheme for band representations as given by Eqs. (1)–(3) one starts with a vectorial representation of the point group T_d around the origin. This representation is labeled Γ_5 in Refs. [4,17,18]. The band representation of O_h^7 that this vectorial representation of T_d induces is denoted by $(a,4)$ in Ref. [8], where a full listing is also given for the symmetries of Bloch functions at different points in the Brillouin zone (called the continuity chord in Ref. [8]). Such a listing is readily obtained when the band representation $(a,4)$ (which is highly reducible) is reduced into irreducible representations of the space group O_h^7. We can now go about proving that the six-branch phonon spectrum which corresponds to the $(a,4)$-band

TABLE I. Wyckoff positions and their little groups for diamond and hexagonal close packed structures. All the positions listed in this table lead to six-branch phonon spectra.

Diamond structure			Hexagonal close packed structure		
Wyckoff position	Little group	Coordinates of Wyckoff position	Wyckoff position	Little group	Coordinates of Wyckoff position
a	$T_d(\bar{4}3m)$	$(0,0,0)$, $(\frac{3}{4},\frac{1}{4},\frac{3}{4})$	c	$D_{3h}(\bar{6}m2)$	$(\frac{1}{3},\frac{2}{3},\frac{1}{4})$, $(\frac{2}{3},\frac{1}{3},\frac{3}{4})$
b	$T_d(\bar{4}3m)$	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$	d	$D_{3h}(\bar{6}m2)$	$(\frac{1}{3},\frac{2}{3},\frac{3}{4})$, $(\frac{2}{3},\frac{1}{3},\frac{1}{4})$

representation extends continuously in frequency from zero to some $\omega_{\max}$. In Table II we list the irreducible representations at the Γ, Δ, and X points in the Brillouin zone that are contained in the $(a,4)$-band representation of O_h^7. Just by considering these three symmetry points one can tell that there are no gaps in the frequency spectrum. This is seen in the following simple way, which is based on symmetry and continuity. At the Γ point we have two three-dimensional representations (see Table II), one for the acoustic branch (Γ_{10}) and one for the optic branch (Γ_4). At the X point there are three two-dimensional representations $X_1X_3X_4$ (see Table II). Going continuously from the acoustic and optic branches (together six in number) to the three double branches at the point X, one necessarily comes to the conclusion that the phonon spectrum is a continuum. This statement is demonstrated in Fig. 1 and in many publications on the phonon dispersion relations for diamond structure crystals [3,11–13]. The above continuity argument is essentially an arithmetic observation of the fact that for two triple lines at Γ to go over into three double lines at X, two single lines emerging from the different Γ representations have to converge at X.

Previously, the Wyckoff position a for O_h^7 was considered. An identical analysis can be carried for the position b with the same result that the six-branch phonon spectrum originating from this position forms a continuum in frequency. In fact, either position a or position b [which differ by a translation $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$] can be used to represent the diamond structure.

We now turn to the hexagonal close packed structure with the D_{6h}^4 ($P6_3/mmc$) space group. This structure is formed by putting ions in either position c or d of D_{6h}^4 (see Ref. [15]). In what follows we consider in detail the Wyckoff position c. The same analysis hods for position d. The decomposition in Eq. (2) for the D_{6h}^4 space group with respect to the position c is

$$D_{6h}^4 = TD_{3h}(c_1) + TID_{3h}(c_1), \tag{5}$$

where I is the inversion and $D_{3h}(c_1)$ is the point group symmetry of the site $c_1 = (\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. As in the case of the above construction for O_h^7, we start with a vectorial representation of the point group D_{3h}. In this case, however, such a representation is reducible and it consists of the representations which are denoted by Γ_4 and Γ_6 in Ref. [17] and by five and three, respectively, in Ref. [18]. The reason that for phonons these two representations have to be considered together is because for the wave vector $\mathbf{k} = 0$ the three acoustic phonons are degenerate at zero frequency. By starting with representations 3 and 5 of the point group D_{3h} around the Wyckoff position c, the construction process of band representations as outlined in the Eqs. (1)–(3) will lead to the band representations $(c,3)$ and $(c,5)$. In Table II we list the irreducible representations at the Γ, Δ, and A points in the Brillouin zone that are contained in the $(c,3)$ and $(c,5)$ band representations of D_{6h}^4. The information in Table II is taken from Ref. [14]. By using symmetry and continuity one can show that there are no gaps in the frequency spectrum corresponding to these two band representations. The representations Γ_6 and Γ_{11} are two dimensional and so are also the representations Δ_5 and Δ_6. The representation A_1 is two dimensional, while A_3 is four dimensional. Δ_1 and Δ_3 are one dimensional. In view of the fact that Γ_8 and Γ_{11} have to coincide at zero frequency, and also in view of the compatibility of Δ_5 with Γ_{11} and Δ_6 with Γ_6, one deduces that the phonon spectrum for the c Wyckoff position forms necessarily a continuum [11–13] (see Fig. 1). A similar analysis can be carried out for the Wyckoff position d of the D_{6h}^4 space group. This concludes the proof of the continuity rule for phonon spectra in diamond and hexagonal close packed structures. There are actually more crystals with two atoms in a unit cell that show the same continuity rule. As examples we quote the following three cubic space groups [19]:

$$T_h^4, \qquad O_h^4, \qquad O_h^6. \tag{6}$$

On the other hand, for crystals with two different atoms in a unit cell the situation is different. For such crystals the phonon spectra belong to two distinct band representations that are induced from vectorial representations at the different atoms. There is no longer continuity that follows from a single band representation, and, in general, phonon spectra for crystals with two different atoms in a unit cell may have gaps [11–13].

In summary, we have shown in this Letter that crystals with diamond and hexagonal close packed structures have

TABLE II. Content of the band representations $(a,4)$ and $(b,4)$ of O_h^7 and of the band representations $(a,3)$, $(a,5)$; $(b,3)$, $(b,5)$; $(c,3)$, $(c,5)$; and $(d,3)$, $(d,5)$ of D_{6h}^4 in their irreducible representations for some symmetry points in the Brillouin zone. Notations are from Ref. [18].

Diamond structure			Hexagonal close packed structure		
Symmetry point in Brillouin zone	Little group	Symmetries of Bloch functions for $(a,4)$ and $(b,4)$	Symmetry point in Brillouin zone	Little group	Symmetries of Bloch functions for $(c,3)$, $(c,5)$; $(d,3)$, $(d,5)$
Γ	O_h	Γ_4, Γ_{10}	Γ	D_{6h}	$\Gamma_3, \Gamma_6, \Gamma_8, \Gamma_{11}$
Δ	C_{4v}	$\Delta_1, \Delta_4, (2\Delta_5)$	Δ	C_{6v}	$\Delta_1, \Delta_3, \Delta_5, \Delta_6$
X	D_{yh}	X_1, X_3, X_4	A	D_{6h}	A_1, A_3

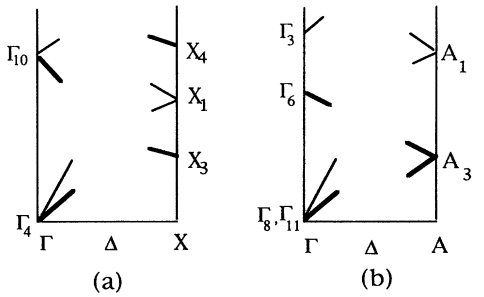

FIG. 1. Diagram of the degeneracies at symmetry points in the Brillouin zone. A thin line is for nondegenerate states; a thick line for doubly degenerate states. (a) For diamond structure; (b) for hexagonal close packed structure. Notations follow Refs. [8,16,18].

a phonon spectrum that extends from zero to some maximal frequency in a continuous way. This continuity feature is present in many other cubic and hexagonal crystals. One of the reasons for this continuity is that phonon spectra have an additional symmetry which is absent for electrons. At zero frequency there are always three phonon branches that coincide because of space homogeneity. Thus, for hexagonal close packed structures the vectorial representation at the Γ point is reducible, and nevertheless for phonons all three acoustic branches have zero frequency at this point. The gapless structure of the phonon spectrum in hexagonal close packed crystals is related to the vanishing of the frequency for the three acoustic branches. Our final remark is about the cubic groups T_h^4 $(Fd\bar{3})$ and O^4 $(F4,32)$ in the list of Eq. (6). The relevant Wyckoff positions for the phonon spectra are the positions a and b with the little group T. As was shown in Ref. [9] the band representations (a,j) and (b,j) for $j = 1,2,3,4$ have the same continuity chords. j labels the irreducible representations of T and $j = 4$ is the vectorial representation of T. What this means is that phonon spectra for the band representations $(a,4)$ and $(b,4)$ will be indistinguishable from the point of view of their symmetries for the Bloch functions at all points in the Brillouin zone. They can, however, be distinguished topologically by means of the open path geometrical phase [20].

It is to be pointed out that for electrons the vectorial representation at Γ of D_{3h} should be considered as consisting of two separate irreducible representations Γ_8 and Γ_{11} with no touching as in Fig. 1(b). Correspondingly, one should expect for electrons two separate bands—one induced from Γ_8 and one from Γ_{11}.

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