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Eduardo C. Marino
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Independent Electrons and Static Crystals

The expression "condensed matter" refers to materials that are either in a solid or in a liquid state. Soon after the atomic theory was established, the structure of matter in these condensed forms became the object of study under that new perspective. These early investigations already revealed that a large amount of the solids, interestingly, exhibit a peculiar structure, which is called a crystal. These rich forms of matter surprisingly assemble their constituent atoms or molecules in such a way that the most stable configuration has a periodic character, namely, there exists a basic unit that repeats itself along the whole sample. The specific geometric form of the periodic crystalline structure is determined by the spatial orientation of the atomic or molecular valence orbitals of the basic components of each crystal material. The existence of this periodic geometric array exerts a profound influence upon the physical properties of the material. These include the energy spectrum, charge and heat transport, specific heat, magnetic and optical properties. The study of crystal lattices, consequently, is of fundamental importance in the physics of condensed matter.

1.1 Crystal Lattices

The mathematical concept that most closely describes an actual crystal lattice is that of a Bravais lattice, a set of mathematical points corresponding to the discrete positions in space given by

$$\{\mathbf{R}|\ \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3;\ n_i \in \mathbb{Z}\}, \tag{1.1}$$

where $\mathbf{a}_i$, $i = 1, 2, 3$ are the so-called primitive vectors in three-dimensional space. The corresponding structure in one(two)-dimensional space would be analogous to (1.1), but having only one(two) primitive vector(s). We can see that the points in the Bravais lattice form a pattern that repeats itself periodically. A characteristic feature of this type of mathematical structure is that it looks exactly the same from the perspective of any of its points $\mathbf{R}$.

The Bravais lattice is invariant under the operation

$$\mathbf{R} \to \mathbf{R} + \mathbf{T}, \tag{1.2}$$

where

$$\mathbf{T} = L\mathbf{a}_1 + M\mathbf{a}_2 + N\mathbf{a}_3, \tag{1.3}$$

and L, M, N are arbitrary but fixed integers. Indeed, clearly for any $\mathbf{T}$ we have $\{\mathbf{R}\} \equiv \{\mathbf{R} + \mathbf{T}\}$, hence translations by $\mathbf{T}$ are symmetry operations of the Bravais lattice. Examples of two-dimensional Bravais lattices are the square lattice and the triangular lattice, see Figs. 1.1 and 1.2.

A useful concept related to a Bravais lattice is that of a primitive unit cell. This is a region of space containing a single point of the Bravais lattice that will cover the whole volume (area in two dimensions, length in one dimension) encompassed by the lattice when translated by all the symmetry operations $\mathbf{T}$, in such a way that these translations do not produce any superpositions. There are in general different regions, with many possible shapes, that satisfy the previous definition. Surprisingly, however, the volume (area in two dimensions, length in one dimension) of all primitive unit cells is always the same, irrespective of their

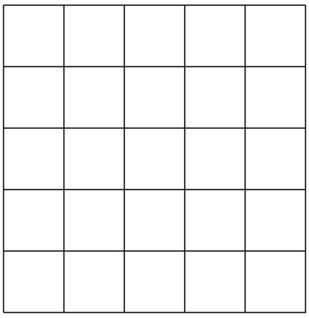

Figure 1.1 Square Lattice: an example of a 2d Bravais lattice

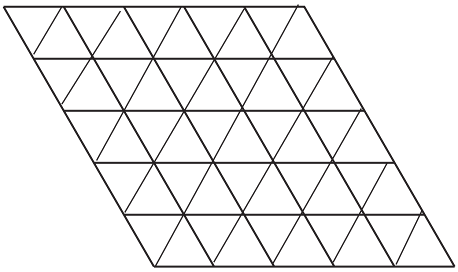

Figure 1.2 Triangular Lattice: an example of a 2d Bravais lattice

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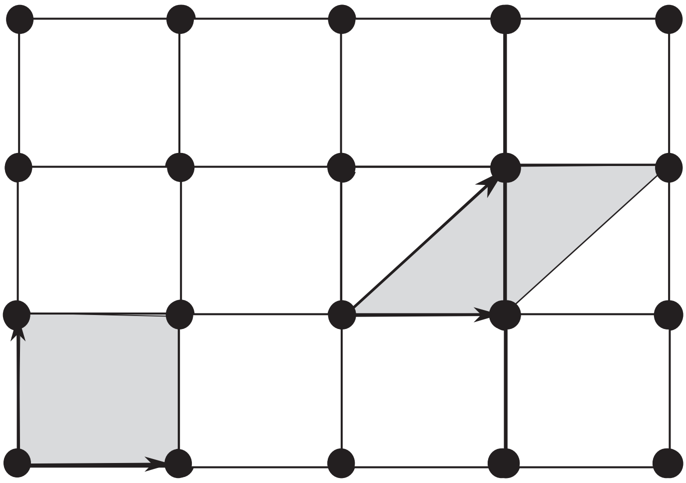

Figure 1.3 Two choices of primitive unit cells for a square lattice, corresponding to different sets of primitive vectors, according to (1.4). Notice that the areas of the two unit cells are, evidently, the same.

specific shape. Evidently, from the definition, the volume V_0 of any primitive unit cell, for a lattice containing N points and a volume V, must be given by $V_0 = \frac{V}{N}$. The mentioned property then follows.

Given a set of primitive vectors, an obvious choice among the many possible primitive unit cells would be

$$\{\mathbf{R}|\ \mathbf{R} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3;\ \ x_i \in [0, 1]\}. \tag{1.4}$$

From this we may infer that the volume of any primitive unit cell is given by

$$V_0 = \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2). \tag{1.5}$$

For two-dimensional lattices, the corresponding area would be

$$A_0 = |\mathbf{a}_1 \times \mathbf{a}_2|, \tag{1.6}$$

whereas for a one-dimensional lattice, we would have the corresponding length

$$L_0 = |\mathbf{a}_1|. \tag{1.7}$$

A crystal structure in general is not just a Bravais lattice; rather it is obtained from the latter by placing what is called a base in each of its points. The base is a finite set of points occupying fixed positions with respect to each of the points of the Bravais lattice.

The so-called honeycomb lattice is an example of a crystal structure, that is not a Bravais lattice. This can be inferred from the fact that points A and B have

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different perspectives of the lattice, as we can see in Fig. 1.4. This crystal structure is obtained by adding to each point of a triangular Bravais lattice having primitive vectors of length a, a base of two points at $(0, 0)$ and $(h, 0)$, with $h = a/\sqrt{3}$.

The actual crystal material is modeled by placing atoms, ions, molecules or radicals in each of the points of a base $\mathcal{B}$ in a Bravais lattice $\mathcal{BL}$. The crystal mass density distribution is then given by

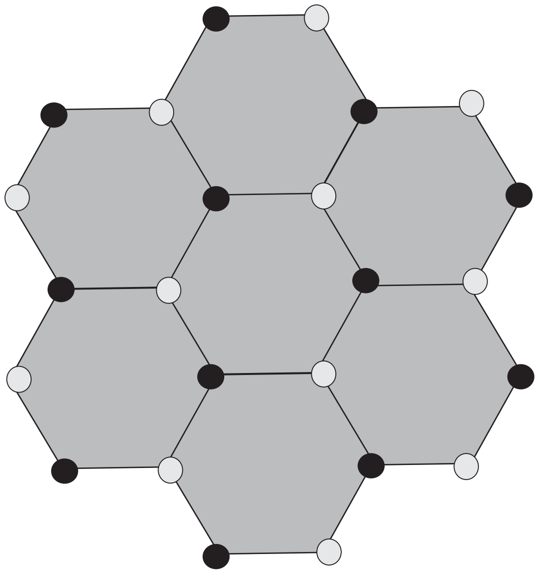

Figure 1.4 Honeycomb crystal structure, showing the two interpenetrating Bravais triangular sublattices A and B, respectively, with black and white dots. Different perspectives of the lattice are clearly obtained from sublattice points A and B.

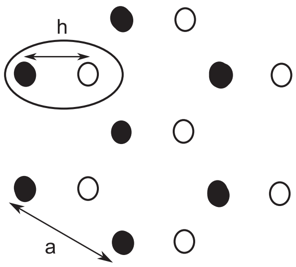

Figure 1.5 Honeycomb crystal structure, showing one Bravais triangular sublattice (black dot with spacing a) and the base (one black and one white dot with spacing $h = a/\sqrt{3}$)

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$$\rho(\mathbf{X}) = \sum_{\mathbf{R}\in\mathcal{BL}} \sum_{i\in\mathcal{B}} m_i \, \delta(\mathbf{X} - \mathbf{R} - \mathbf{r}_i), \tag{1.8}$$

where m_i is the mass of the constituent at the point $\mathbf{R} + \mathbf{r}_i$ of the crystal structure. One can verify that the above expression is invariant under the $\mathcal{BL}$ symmetry operations (1.3), namely,

$$\rho(\mathbf{X}) = \rho(\mathbf{X} + \mathbf{T}), \tag{1.9}$$

which follows from the fact that $\sum_{\mathbf{R}} = \sum_{\mathbf{R}-\mathbf{T}}$ for $\mathbf{R} \in \mathcal{BL}$.

In the next section we will study the Fourier expansion of periodic quantities possessing the Bravais lattice symmetry (1.9) and shall explore the important consequences of this condition.

1.2 The Reciprocal Lattice

Let $f(\mathbf{X})$ be a periodic physical quantity exhibiting the same symmetry as a given Bravais lattice, namely

$$f(\mathbf{X}) = f(\mathbf{X} + \mathbf{R}). \tag{1.10}$$

An example of such a quantity is the crystal mass distribution function $\rho(\mathbf{X})$, introduced in (1.8).

The invariance of a function $f(\mathbf{X})$ under translations by Bravais lattice points manifests itself in its Fourier expansion as

$$\begin{aligned} f(\mathbf{X}) &= \sum_{\mathbf{q}} f(\mathbf{q}) \exp\{i\mathbf{q}\cdot\mathbf{X}\} \\ &= \sum_{\mathbf{q}} f(\mathbf{q}) \exp\{i\mathbf{q}\cdot(\mathbf{X}+\mathbf{R})\}, \end{aligned} \tag{1.11}$$

which implies

$$\mathbf{q}\cdot\mathbf{R} = 2\pi n \quad ; \quad n \in \mathbb{Z}. \tag{1.12}$$

This relates the position vectors of a certain Bravais lattice to the argument of the Fourier transform of *any* function having the same symmetry of such a lattice.

Considering that $\mathbf{R} = \sum_i n_i \mathbf{a}_i$, according to (1.1), we see that the above relation is solved by

$$\mathbf{q} = \sum_j l_j \mathbf{b}_j \quad ; \quad l_j \in \mathbb{Z}, \tag{1.13}$$

provided the vectors $\mathbf{b}_j$ satisfy the following relation with the primitive vectors of the Bravais lattice,

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}. \tag{1.14}$$

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Indeed, this implies

$$\mathbf{q} \cdot \mathbf{R} = 2\pi \left(\sum_i n_i \, l_i \right) \quad ; \quad n_i, l_i \in \mathbb{Z}, \tag{1.15}$$

and it is easy to see that the quantity between parentheses above is an integer. We conclude, therefore, that (1.13) with the condition (1.14) satisfies (1.12).

The solution of (1.14) for the vectors $\mathbf{b}_i$ in three dimensions would be

$$\mathbf{b}_1 = \left(\frac{2\pi}{V_0} \right) \mathbf{a}_2 \times \mathbf{a}_3, \tag{1.16}$$

where V_0 is given by (1.5). The vectors $\mathbf{b}_2$ and $\mathbf{b}_3$ are obtained by cyclic permutations. An example in two dimensions would be the square lattice, for which the solution of (1.14) would be

$$\mathbf{b}_i = 2\pi \, \frac{\mathbf{a}_i}{|\mathbf{a}_i|^2} \quad , \quad i = 1, 2. \tag{1.17}$$

For a one-dimensional lattice, the solution of (1.14) would be

$$\mathbf{b}_1 = 2\pi \, \frac{\mathbf{a}_1}{|\mathbf{a}_1|^2}. \tag{1.18}$$

The set of vectors $\mathbf{q}$ in (1.13) clearly form themselves a Bravais lattice with primitive vectors $\mathbf{b}_i$, namely

$$\{\mathbf{Q} | \; \mathbf{Q} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3; \; n_i \in \mathbb{Z}\}. \tag{1.19}$$

This is called “reciprocal lattice,” a name derived from the fact that the vectors $\mathbf{b}_i$ have dimension of inverse length, whereas the corresponding vectors of the original lattice, namely $\mathbf{a}_i$ have dimension of length. Notice that there is only one reciprocal lattice associated to a given Bravais lattice and that the latter is the reciprocal of the former.

The Fourier components of a periodic function possessing the same symmetry of a certain Bravais lattice only depend on wave-vectors, which belong to the corresponding reciprocal lattice. This fact has deep consequences, as we shall see. For instance, the Fourier transform of a function satisfying (1.10), for a certain Bravais lattice $\{\mathbf{R}\}$,

$$f(\mathbf{Q}) = \int_V d^3X f(\mathbf{X}) \exp\{-i\mathbf{Q} \cdot \mathbf{X}\}, \tag{1.20}$$

becomes after making $\mathbf{X} = \mathbf{r} + \mathbf{R}$, $\int_V = \sum_{\mathbf{R}} \int_{V_0}$

$$f(\mathbf{Q}) = \sum_{\mathbf{R}} \int_{V_0} d^3r f(\mathbf{r} + \mathbf{R}) \exp\{-i\mathbf{Q} \cdot (\mathbf{r} + \mathbf{R})\}$$

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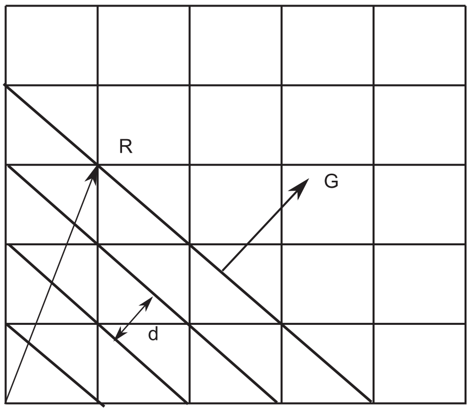

Figure 1.6 Reciprocal lattice vectors **G** are the director-vectors of a family of planes in the original Bravais lattice, spaced by d, according to Eq. (1.22).

$$= N \int_{V_0} d^3 r f(\mathbf{r}) \exp\{-i\mathbf{Q}\cdot\mathbf{r}\}, \tag{1.21}$$

where N is the number of points/cells in the Bravais lattice. The last step follows from the symmetry of the function and the fact that **Q** belongs to the reciprocal lattice. We see that the relevant integral sweeps the primitive unit cell only.

The vectors in the set $\{\mathbf{Q}\}$ have an interesting and important feature in connection to its associated Bravais lattice. It is not difficult to see that any Bravais lattice contains different (infinitely many) sets of parallel planes separated by a distance d. The subset of vectors of the Bravais lattice belonging to the nth plane of such set satisfy the relation

$$\mathbf{R}\cdot\frac{\mathbf{G}}{|\mathbf{G}|} = nd \quad ; \quad n \in \mathbb{Z}, \tag{1.22}$$

where **G** is a vector perpendicular to this family of planes. By choosing $|\mathbf{G}| = \frac{2\pi}{d}$, we see that (1.22) reduces to (1.12). We then may infer that the director-vectors **G** are just the elements of the reciprocal lattice (1.19). Each of the vectors **Q** in (1.19), therefore, determines a family of parallel planes in the Bravais lattice, orthogonal to it and such that the basic spacing between adjacent planes is $d = \frac{2\pi}{|\mathbf{Q}|}$.

Let us turn now to a concept that is of foremost importance in the reciprocal lattice. That is the Wigner–Seitz primitive unit cell. This is defined by a peculiar choice of the cell boundary, which is obtained according to the following method. For each of the lattice points, draw lines connecting it to its 1st neighbors, 2nd neighbors... (as much as needed), and then take the set of planes (lines in two dimensions) orthogonal to these lines and intersecting them right at the middle. The resulting cell boundary is the closed surface formed by the union of the

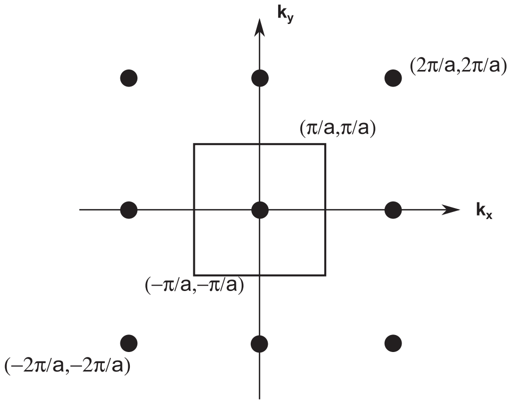

Figure 1.7 The reciprocal lattice of a square lattice with lattice parameter a is a square lattice with spacing $b = \frac{2\pi}{a}$, represented in the figure as black dots. The central square is the First Brillouin zone, the Wigner–Seitz primitive unit cell of the reciprocal lattice.

regions belonging to each of these planes, which form faces. The points of such planes not forming faces of the cell boundary are discarded. The adaptation of this construction to one-dimensional lattices is straightforward.

We have seen that any primitive unit cell has the same volume $\frac{V}{N}$, so this is accordingly the volume of the Wigner–Seitz cell. It can be shown, however, that it is, among all possible primitive unit cells, the one for which the sum of the distances between the cell points and the lattice point it contains is minimal. Another property of the Wigner–Seitz cell is that, by construction, it has the same symmetry as the lattice for which it is defined.

The Wigner–Seitz primitive unit cell of the reciprocal lattice is called the first Brillouin zone. As we shall see, it plays a fundamental role in the quantum-mechanical description of crystalline solids, having profound implications upon the electronic properties of these materials. We shall understand the reason for that in the next section.

The reciprocal lattice also plays an important role in connection with the pattern of x-ray scattering by a crystal. When electromagnetic radiation of wavelength λ falls upon a crystal, the waves reflected by adjacent planes of the Bravais lattice undergo constructive interference whenever the Bragg condition is satisfied, namely

$$2d \sin\theta = n\lambda \quad ; \quad n \in \mathbb{N}, \tag{1.23}$$

where d is the interplane spacing for a family of parallel planes, and θ, the angle between these planes and the direction of the incident radiation (see Fig. 1.9). This,

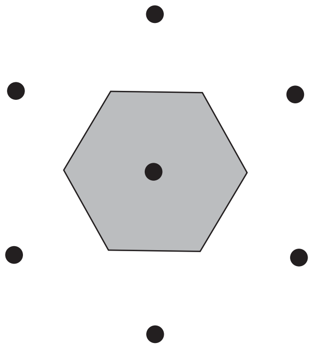

Figure 1.8 Reciprocal lattice of a triangular lattice. The shaded area is the First Brillouin zone.

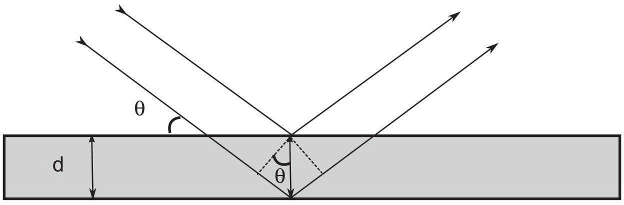

Figure 1.9 Interference between waves scattered from adjacent planes with spacing d, leading to the Bragg condition. The difference in the optical paths of the two beams is $2d \sin\theta$.

of course, will only occur at significative angles when λ is comparable to $d \simeq 0.1$nm, which corresponds to the x-ray region.

The process of reflection of electromagnetic radiation by a crystalline solid may be formulated equivalently as the quantum-mechanical elastic scattering of photons by a periodic potential, which has the same symmetry as the Bravais lattice of the crystal. The probability amplitude for an incident photon with wave-vector $\mathbf{k}_i$ to be scattered into a final state with wave-vector $\mathbf{k}_f$ is given, in first-order Born approximation, by an expression proportional to

$$\langle \mathbf{k}_f | V(\mathbf{r}) | \mathbf{k}_i \rangle = \int d^3 r e^{-i(\mathbf{k}_f - \mathbf{k}_i)\cdot \mathbf{r}} V(\mathbf{r}). \tag{1.24}$$

This is the Fourier transform of the potential, which can be written as

$$V(\mathbf{r}) = \sum_{\mathbf{R}\in\mathcal{BL}} \sum_{i\in\mathcal{B}} v_i(\mathbf{r} - \mathbf{R} - \mathbf{r}_i). \tag{1.25}$$

This has the symmetry of the Bravais lattice, Eq. (1.10), and consequently it follows that

$$\mathbf{k}_f - \mathbf{k}_i = \mathbf{Q} \tag{1.26}$$

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is a vector of the reciprocal lattice. Using this fact and making the change of variable $\mathbf{r} \to \mathbf{r} - \mathbf{R} - \mathbf{r}_i$ we see that

$$\langle \mathbf{k}_f | V(\mathbf{r}) | \mathbf{k}_i \rangle = N \sum_{i \in \mathcal{B}} v_i(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{r}_i}, \tag{1.27}$$

where the sum is over the base points. When this has just a single point, we would have

$$\langle \mathbf{k}_f | V(\mathbf{r}) | \mathbf{k}_i \rangle = N\, v(\mathbf{Q}), \tag{1.28}$$

and when all the base points are occupied by identical constituents,

$$\langle \mathbf{k}_f | V(\mathbf{r}) | \mathbf{k}_i \rangle = N\, v(\mathbf{Q}) \sum_{i \in \mathcal{B}} e^{-i\mathbf{Q}\cdot\mathbf{r}_i} \equiv N\, v(\mathbf{Q}) S(\mathbf{Q}). \tag{1.29}$$

Notice the presence of the "geometric form factor," $S(\mathbf{Q})$, whenever the base has more than one point. In the three previous equations, $\mathbf{Q}$ is given by (1.26), a relation known as the von Laue condition. If we square it and use the fact that for elastic scattering $|\mathbf{k}_f| = |\mathbf{k}_i| = \frac{2\pi}{\lambda}$, that $|\mathbf{Q}| = \frac{2\pi}{d}$ for reciprocal lattice vectors, and that the angle between the incident and reflected wave-vectors is 2θ, we can immediately show that (1.26) is just the first Bragg condition for constructive interference. Hence the first-order Born approximation gives the first Bragg peak, which will have an intensity proportional to the squared modulus of the amplitude (1.27).

X-ray spectroscopy constitutes a powerful instrument for the investigation of the structural properties of crystalline solids. In an x-ray experiment, the peaks in the reflected beam will occur right at $\mathbf{k}_i + \mathbf{Q}$, with an intensity proportional to $|v(\mathbf{Q})|^2$, with a possible additional modulation by the geometrical form factor. We conclude that the peaks in the interference spectrum occurring in the x-ray scattering by a crystal provide a direct mapping of the reciprocal lattice of this crystal. The intensity of these peaks will bring information about the local potential v.

In the next section, we explore the consequences of a crystalline structure on the electronic properties of the material.

1.3 Independent Electrons in a Periodic Potential

We will consider here the behavior of electrons in the presence of a periodic potential possessing the same symmetry as a given Bravais lattice. In this first approach we shall neglect the interactions of the electrons among themselves as well as the deviations from an ideal lattice, due, for instance, to thermal and quantum fluctuations. Such periodic potential is created by the basic constituents of the crystal, which are localized at each of the points of the crystalline structure. Its general form is given by (1.25).

The consequences of the presence of a periodic potential in a crystal are of foremost importance for the description of the electronic properties in a crystalline