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Symmetry of periodically distorted crystals

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Recently one has seen a growing interest in systems, like modulated crystals and crystals with charge or spin density waves, which can be considered as crystals with a distortion which is periodic in space or in space time. The Euclidean symmetry of these systems is, in general, not a three-dimensional space group and is fairly low. It is shown that enlarging the admitted group of transformations the symmetry group is a space group with dimension higher than three. For static systems the additional dimensions are related to internal degrees of freedom associated with relative Euclidean motions of the distortion with respect to an average crystal structure and for time-dependent ones to the time. A discussion of the symmetry is given, both for point particle systems and for continuous density distributions. These higher-dimensional space groups are relevant for the physical properties of such crystals, as shown here in particular for systematic extinctions occurring in their diffraction patterns.

I. INTRODUCTION

For a long time the three-dimensional space-group symmetry of a perfect crystal has been considered as one of the main characteristics of the solid state. From this, important consequences for the physical properties follow. However, in recent years one has increasingly become interested in condensed-matter systems without this three-dimensional space-group symmetry. Examples are a number of systems (some of them given in Appendix A) which can be considered as a perfect crystal with a deviation, in the sense that the deviation itself has symmetry properties, e.g., it is a periodic distortion. In this way the system has in general a lower Euclidean symmetry, but is still perfectly ordered. This latter feature is revealed by the sharpness of the spots in the (x-ray, electron, or neutron) diffraction pattern.

The presence of periodic crystal distortions can be seen in the diffraction pattern from so-called *satellite reflections*. These are associated with peaks in the diffracted intensity distribution in the reciprocal space regularly distributed around (and generally weaker than) the so-called *main reflections*. This explains the name. Conversely the presence of satellite reflections can be interpreted as due to periodic distortions associated with density and/or displacive wave deviations from an undistorted crystal structure called *basic structure*[1] (in Ref. 2 the name "reference structure" is used). This basic structure is not always uniquely determined by the diffraction pattern. In many cases it has the same symmetry group as that of the crystal at a temperature just above the appearance of the satellite reflections. But there is not always an undistorted state corresponding to the basic structure.

The distinction between satellites and main reflections cannot be made on the basis of intensity only. Satellites stronger than corresponding main reflections can very well occur. Furthermore the deviations from the basic structure need not to be small. Nevertheless in all practical cases known, the identification of the main reflections gives no problem. In some cases the determination of the basic structure is not as easy, as will be discussed further on. Therefore another structure is considered more directly related to the diffraction pattern: that of *average structure*. This is the structure one obtains by disregarding satellites and by taking into account the main reflections only. The real distorted state then appears as the result of a structure refinement with respect to the average structure. Note that both average structure and basic structure are invariant under the same group of discrete space translations, generating a three-dimensional lattice Λ_3, so that their symmetry (which in general is not the same) is given by a (three-dimensional) space group. If this is the case for the (periodically) distorted crystal, the latter is said to form a *superstructure* (of the basic one). Characteristic for a superstructure is the fact that with respect to the reciprocal lattice Λ_3^* of the basic structure, the satellites occur with rational indices. Equivalently one can say that such satellites belong to a lattice Σ_3^* containing Λ_3^*. The index of Λ_3^* in Σ_3^* expresses the number of times the elementary cell of the basic structure is contained in that of the superstructure. In the case of *long-period structures* this number is large compared to one.

There are crystals in which the positions of the satellite reflections vary continuously with respect to Λ_3^* as a function of the temperature (in a given temperature interval). Interpretation of such a diffraction pattern in terms of three-dimensional space groups is possible, but not meaningful, because it would require for that given temperature interval an arbitrarily large number of different superstructures, whose elementary cells would mostly be of macroscopic dimension. Much simpler is the situation if one admits satellites incommensurable with the main reflections, i.e., nonrational indices. The corresponding crystal is then characterized by a periodic distortion incommensurable with respect to the basic structure and has a so called *modulated crystal structure*.[2] Clearly the symmetry group of a modulated crystal cannot be a three-dimensional space group, as the unit cell has an infinite volume. The aim of the present paper is to show how, by considering additional dimensions and operations, the symmetry of periodically distorted crystals can still be described by crystallographic space groups (of dimension larger than three).

One has to distinguish between whether or not the distortion is a time-dependent or a static one. In the time-dependent case considered here, time is the additional dimension required: the symmetry of the distorted crystal is in fact the space-time symmetry of its world lines. In the time-independent case the relative positions of the periodic distortion with respect to a basic structure can be associated with internal degrees of freedom of the system considered as a two-component system: the additional dimensions are used to describe the (Euclidean) relative motions of one component (the deformation) with respect to the other (the basic structure). So the product space is here maximally of dimension six.

This situation is comparable with that one finds in molecules having a degenerate ground state in the Born-Oppenheimer approximation, where also internal degrees of freedom are used for describing relative motion of subsystems.[3] One can indeed show that, e.g., in the case of incommensurate deformations (modulated crystals) the ground state of the system is also degenerate for shifts of the deformation relative to the basic structure. In both cases these crystallographic groups of dimension higher than three are physically relevant: in particular, they allow for a simple formulation of *extinction rules* for diffraction, which are the result of correlations between atoms in the crystal not simply expressible in terms of Euclidean symmetries in the three-dimensional space. The bigger the supercell, the more useful can be this approach.

Before going into details let us briefly discuss different types of periodic distortions: periodic lattice distortions and periodic density distortions.

The periodic lattice distortion is conceptually the simplest case: the distortion is of the *displacive type*. The distorted structure is obtained by periodic displacement from the corresponding positions in the basic structure. Superstructure formation of the displacive type is typical for many structural phase transitions, in particular for the ferroelectric or antiferroelectric ones. The case of the displacive modulated crystal γ-Na_2CO_3 has been analyzed in detail by de Wolff and his collaborators.[4] Furthermore, any crystal vibrating in a single normal mode (of nonzero frequency) shows a lattice distortion periodic in time and, at any fixed time, periodic in space.

The description of a distorted crystal by means of displacements with respect to a basic structure becomes rather an arbitrary one if the relevant distribution function is not sharply peaked, i.e., if the point-particle approximation is not a good one. An extreme example is that of a crystal where the conduction electrons are considered to move nearly free in a jelliumlike medium: the relevant distribution function is then a charge density or a spin density that is nearly constant. The periodic distortions that may occur, in the well-known form of charge-density waves (CDW) and spin-density waves (SDW), respectively, can hardly be seen as displacements from an undistorted basic structure, even if they can produce a periodic lattice distortion. The same can be said in the case of solid solutions (as in alloys) where the position of a given atom is described in terms of a probability function attached to given crystallographic positions and where periodic deviation from a uniform distribution is expressible in terms of *concentration or occupation probability waves*. Quite generally, these density waves also give rise to satellite reflections, but that can be distinguished from those due to displacive waves.[1] Very often distortions of various type occur together. In some of these cases the concept of basic structure is still a natural one, in others not. In all cases, however, the concept of average structure can be used. Even if this last is sometimes more difficult to be visualized, the average structure shares many of the useful symmetry properties of the basic structure.

In the following, the same problem, that of a suitably defined symmetry of a periodically distorted crystal, is considered from different point of views, depending on the type of distortion and on the way the crystal is described. Time-dependent distortions are considered in Secs. II and V, static ones in Secs. III and IV. The following two sections are based on a pointlike atomic description of the crystal, the last two on that by means of a density function. Appendixes give more detailed information on some specific points.

II. PHONON-TYPE SYMMETRY

In crystal physics many different elementary excitations occur which transform according to irreducible representations of the space group of the crystal under consideration.[5] The knowledge of the symmetry group of a given elementary excitation is helpful when constructing normal coordinates.[6] But usually, since many different elementary excitations occur at the same time, only the symmetry group of the ground state is the relevant one. There are situations, however, where one mode (or a given set of modes) plays a dominant role, is occupied macroscopically, and gives rise to collective phenomena producing as a new ground state, that of a distorted crystal.[7]

As a typical example we consider a crystal undergoing a structural phase transition induced by a so-called soft phonon, just above the critical temperature. The symmetry of the crystal driven by such a vibrating normal mode is relevant for that of the crystal in the distorted phase. We will show that, indeed, such a relation is expressible in group theoretical terms. (The general situation, however, deserves further investigation.) Moreover, in such a situation the macroscopically occupied soft phonon state does not represent anymore an elementary excitation: the ground state of the crystal is no more the static one but that of a crystal vibrating according to the corresponding critical mode. Consequently its elementary excitations should transform according to irreducible representations of the symmetry group of the vibrating crystal, a point of view that we hope to analyze in a subsequent paper.

The model adopted here is that of a harmonic point particle crystal vibrating in a single normal mode.[8] Our system is thus a periodically distorted crystal, and the basic structure is that of the particles at their equilibrium positions. We denote by X_0 the mass distribution and by G_0 the space group of this basic structure.

The distribution X_0 can be written

$$X_0 = \sum_{\vec{n}j} m_j \delta(\vec{r} - \vec{r}_0(\vec{n},j)),$$

where

$$\vec{r}_0(\vec{n},j) = \vec{n} + \vec{r}_j, \quad \vec{n} \in \Lambda_3, \tag{2.1}$$

and $j = 1, 2, \ldots, s$ labels the atoms with mass m_j in a unit cell of the three-dimensional lattice Λ_3. The space group G_0 is defined as

$$G_0 = \{g \in \mathrm{E}(3)\,|\,gX_0 = X_0\}, \tag{2.2}$$

where E(3) is the Euclidean group of the three-dimensional space V_3. For the elements of G_0 we write as usual $g = \{R\,|\,\vec{a}\}$. The vibrating crystal is described by the space-time distribution

$$\tilde{X} = \sum_{\vec{n}j} m_j \delta(\vec{r} - \vec{r}(\vec{n},j)_t)$$

in the four-dimensional space-time V_4, where $\vec{r}(\vec{n},j)_t$ denotes the position in space at time t of the particle j with equilibrium position in the unit cell denoted by $\vec{n}$.

Writing

$$\vec{r}(\vec{n},j)_t = \vec{r}_0(\vec{n},j) + \vec{u}(\vec{n},j)_t, \tag{2.3}$$

we see that the world lines described by $\tilde{X}$ determine a time-dependent vector field $\vec{u}$ of displacements with respect to the basic crystal. The motion being harmonic, the time average of all displacements vanishes:

$$\langle \vec{u}(\vec{n},j)_t \rangle \equiv \lim_{T\to\infty} \frac{1}{T} \int_0^T \vec{u}(\vec{n},j)_t \, dt = 0, \tag{2.4}$$

so that

$$\langle \tilde{X} \rangle = X_0. \tag{2.5}$$

The symmetry group G of the vibrating crystal is here defined as

$$G = \{g \in \mathrm{IG}(4)\,|\,g\tilde{X} = \tilde{X}\}, \tag{2.6}$$

where IG(4) denotes the inhomogeneous Galilei group in four dimensions.

The determination of G proceeds in three steps. One first looks for a relation between G and G_0 as a consequence of that between $\tilde{X}$ and X_0 [see (2.5)]. One then looks at the transformation properties of the displacement vector field $\vec{u}$ with respect to G_0, which are known from the classification of the normal modes according to irreducible representations of G_0. Finally, the problem of finding G appears to be one often met when the group of admitted symmetry transformations is enlarged [here from E(3) to IG(4)]: that of determining the so-called *compensating transformations*.[9] In the present case these appear to be time translations.

Indeed, the following lemma shows that in G under conditions usually satisfied in vibrating crystals as described here, only elements belonging to the group E(3) × E(1) occur.

This group generated by the Euclidean motions in space, the time translations and the time reversal, plays an important role in symmetry considerations for many nonrelativistic physical systems, but has not yet received a generally accepted name. We have called it first "generalized magnetic group" and later on "Shubnikov group." Bacry *et al.* proposed the name "Aristotle group" $\mathrm{Ar}^+(3)$ and Opechowski introduced the name "Newton group."

Lemma 1: Consider $\vec{r}(\vec{n},j)_t$ as defined in (2.3). Suppose

$$\langle \vec{r}(\vec{n},j)_t \rangle = \vec{r}_0(\vec{n},j),$$

then the group G leaving invariant $\tilde{X}$ determined by $\vec{r}(\vec{n},j)_t$ is a subgroup of $E(3) \times E(1)$.

Proof: A general element $g = (R, \vec{v}, \vec{a}, \epsilon, \tau) \in IG(4)$ transforms a point $(\vec{r}, t) \in V_4$ into

$$g(\vec{r}, t) = (R\vec{r} + \vec{v}t + \vec{a}, \epsilon t + \tau), \tag{2.7}$$

where $R \in O(3)$, $\vec{a}$ is a space translation, τ a time translation, $\epsilon = \pm 1$ and $\vec{v}$ a velocity vector.

So that for $g \in G$ one has

$$\begin{aligned} g(\vec{r}(\vec{n},j)_t, t) &= (R\vec{r}(\vec{n},j)_t + \vec{v}t + \vec{a}, \epsilon t + \tau) \\ &= (\vec{r}(\vec{n}',j')_{t'}, t'), \end{aligned} \tag{2.8}$$

where $\vec{n}'$, j', and t' depend, in general, on $\vec{n}$, j, t, and g; of course, for the masses one has $m_j = m_{j'}$.

By taking the time average one gets

$$\vec{r}_0(\vec{n}',j') = R\vec{r}_0(\vec{n},j) + \vec{a} + \lim_{T \to \infty} (\tfrac{1}{2}\vec{v}T), \tag{2.9}$$

implying $\vec{v} = 0$. Note that if $\vec{r}(\vec{n},j)_t$ would be defined on points of a space-time lattice only, then (2.8) would only involve discrete values of t and the time average would not be (2.9).

It is because point particle world lines are continuous, that nontrivial (i.e., with $\vec{v} \neq 0$) Galilei transformations are excluded.

According to this lemma we can write the elements of G as elements of $E(3) \times E(1)$ in the form

$$g = (R, 0, \vec{a}, \epsilon, \tau) \equiv (\{R \mid \vec{a}\}, \{\epsilon \mid \tau\}). \tag{2.10}$$

$\{R \mid \vec{a}\}$ is called the space component, and $\{\epsilon \mid \tau\}$ the time component of g. For $\epsilon = 1$, g is orthochronous, for $\epsilon = -1$, it is antichronous.

The projection π: $V_4 \to V_3$, defined by $\pi(\vec{r}, t) = \vec{r}$, induces a homomorphic mapping $\tilde{\pi}$: $E(3) \times E(1) \to E(3)$, defined by

$$\tilde{\pi}(\{R \mid \vec{a}\}, \ \{\epsilon \mid \tau\}) = \{R \mid \vec{a}\}, \tag{2.11}$$

and because of (2.5), (2.8), and (2.9), these last for $\vec{v} = 0$, one has

$$(\tilde{\pi}G)X_0 = X_0, \tag{2.12}$$

implying

$$\tilde{\pi}G \subseteq G_0. \tag{2.13}$$

Therefore the action of G on the vector field $\vec{u}$ is well defined and any symmetry of $\tilde{X}$ is a symmetry of $\vec{u}$; also note that this is not true in general but a consequence of the assumptions appearing in Lemma 1, whereas any symmetry of the vector field $\vec{u}$ is always a symmetry of $\tilde{X}$ (see Fig. 1). Accordingly we can adopt for G the more convenient definition

$$G = \{g \in E(3) \times E(1) \mid g\vec{u} = \vec{u}\}. \tag{2.14}$$

The symmetry condition for $g \in G$ as in (2.10) gets the more explicit form

$$\vec{u}(\vec{n}',j')_{t'} = R\vec{u}(\vec{n},j)_t, \tag{2.15}$$

where the transformed positions are given by

$$t' = \epsilon t + \tau, \quad \vec{n}' + \vec{r}_{j'} = R(\vec{n} + \vec{r}_j) + \vec{a}. \tag{2.16}$$

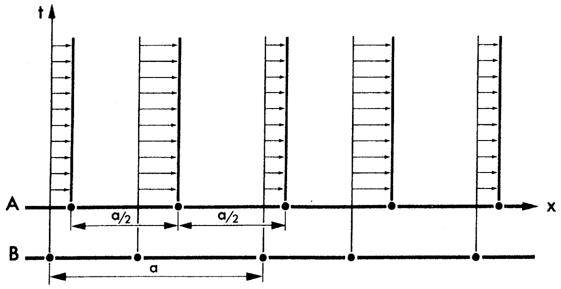

FIG. 1. In this example $\frac{1}{2}\vec{a} \in \tilde{\pi}G$ is a symmetry of the displaced world lines (A) but not of the displacive vector field $\vec{u}$ defined on the positions of the basic structure (B) only ($\frac{1}{2}\vec{a} \notin G_0$).

According to the standard theory of lattice vibrations of a harmonic crystal we write (in the notation used in Ref. 10):

$$\begin{aligned} u_\alpha(\vec{n},j)_t &= \sum_{\vec{q} \in BZ} u_\alpha(\vec{q},j)_t e^{i\vec{q}\vec{n}} \\ &= \sum_{\vec{q}} \sum_{\lambda=1}^{3s} Q^0_{\vec{q}\lambda} e(\alpha j \mid \vec{q}\lambda) e^{i(\vec{q}\vec{n} - \omega_{\vec{q}\lambda} t)} + \text{c.c.}, \end{aligned} \tag{2.17}$$

where $\alpha = 1, 2, 3$ numbers the components of $\vec{u}(\vec{n},j)_t$ with respect to a suitable basis; $Q^0_{\vec{q},\lambda}$ are (complex) normal coordinates; $e(\alpha j \mid \vec{q}\lambda)$ can be seen as entries of a $3s \times 3s$ (complex) matrix, the so-called polarization matrix; and c.c. means complex conjugation.

The case considered here arises when the coefficient of a given mode, say $(\vec{q}, \lambda)$, dominates all the others. It is therefore natural to disregard at first the latter and to consider a system in what we call the single-mode approximation. Improvements can then be obtained either by taking into account the neglected normal mode vibrations by a perturbative treatment, or by considering the vibrational excitations of a crystal whose ground state is that in which the atoms move according to the mode $(\vec{q}, \lambda)$. In both cases it is important to know the symmetry group of the crystal in the single-mode vibrational state. According to (2.13) the spatial component $\tilde{\pi}g = \{R \mid \vec{a}\}$ of an element of G belongs to the space group G_0 of the basic structure.

Let us therefore consider how the normal mode $(\vec{q}, \lambda)$ transforms under such an element. One has[10]

$$(\tilde{\pi}g\cdot\vec{u})_\alpha(\vec{n},j)_t=Q^0_{\vec{q}\lambda}\sum_{\substack{\beta=1,2,3\\ l=1,2,\ldots,s}}\Gamma(\tilde{\pi}g,\vec{q})^{\alpha\beta}_{jl}e(\beta l\,|\,\vec{q}\lambda)\times e^{i(R\vec{q}\cdot\vec{n}-\omega_{\vec{q}\lambda}t)}+\text{c.c.},\tag{2.18}$$

where

$$\Gamma(\{R\,|\,\vec{a}\},\vec{q})^{\alpha\beta}_{jl}=R_{\alpha\beta}\delta_{jl'}e^{-iR\vec{q}\cdot\vec{u}(\tilde{\pi}g,l)},\tag{2.19}$$

with the lattice translation $\vec{u}(\tilde{\pi}g,l)\in\Lambda_3$ determined by

$$R\vec{r}_l+\vec{a}=\vec{r}_{l'}+\vec{u}(\tilde{\pi}g,l),\tag{2.20}$$

and $\delta_{jl'}$ is the Kronecker symbol (see Ref. 10 for more details). Hence the mode $(\vec{q},\lambda)$ transforms into a mode with wave vector $R\vec{q}$ and frequency $\omega_{\vec{q}\lambda}$. Under time reversal the same mode transforms into the mode $(-\vec{q},\lambda)$ with the same frequency $\omega_{\vec{q}\lambda}$. Finally, under a time translation $\{1|\tau\}$ the mode gets a phase shift $\omega_{\vec{q}\lambda}\tau$. Therefore a necessary condition for $g=(\{R\,|\,\vec{a}\},\{\epsilon\,|\,\tau\})$ to be an element of G is given by

$$R\vec{q}\equiv\epsilon\vec{q}(\text{mod}\Lambda_3^*)\quad\text{for }\{R\,|\,\vec{a}\}\in G_0.\tag{2.21}$$

Let us first look at the subgroup G^+ of G formed by its orthochronous elements. Then one has

$$\tilde{\pi}G^+\subseteq G_{\vec{q}}\equiv\{\{R|\vec{a}\}\in G_0\,|R\vec{q}\equiv\vec{q}(\text{mod}\,\Lambda_3^*)\}.\tag{2.22}$$

Therefore $\tilde{\pi}$ projects G^+ on a subgroup of the little group of the wave vector $\vec{q}$. As is well known $G_{\vec{q}}$ is an equitranslational subgroup of G_0 (i.e., both space groups have the same translation subgroup, $U_{\vec{q}}=U_0$). The group $G_{\vec{q}}$ acting on the complexified $3s$-dimensional configuration space M_c spanned by all possible displacements from equilibrium of the atoms in the unit cell of the basic structure (i.e., generated with complex coefficients) defines a unitary representation $\Gamma_{\vec{q}}$ of $G_{\vec{q}}$ by

$$\Gamma_{\vec{q}}(g_0)=\Gamma(g_0,\vec{q}),\quad g_0\in G^+,\tag{2.23}$$

with Γ as in (2.19). This representation can be decomposed into its irreducible components $D^{(\nu)}$:

$$\Gamma_{\vec{q}}(g_0)\cong\Delta(g_0,\vec{q})=\sum_\nu D^{(\nu)}(g_0).\tag{2.24}$$

The polarization vectors labeled by $\lambda=1,2,\ldots,3s$ and with components $e(\alpha j\,|\vec{q}\lambda)$ form a basis of M_c. In the case of natural degeneracy, and after a suitable ordering of these vectors according to the eigenfrequencies, it is precisely by referring the representation $\Gamma_{\vec{q}}$ to this normal mode basis, that one gets the desired reduction. Indeed

$$\Delta(g_0,\vec{q})=e(\vec{q})^{-1}\Gamma(g_0,\vec{q})e(\vec{q}),\tag{2.25}$$

where $e(\vec{q})$ is the $3s\times3s$ polarization matrix whose column vectors are the polarization vectors considered above. Furthermore, each polarization vector belongs to a (unitary) basis of one of the irreducible representations $D^{(\nu)}$ occurring in (2.24). Using (2.25) and because of (2.22) one can write for (2.18)

$$(\tilde{\pi}g\cdot\vec{u})_\alpha(\vec{n},j)_t=\sum_{\mu=1}^{3s}e(\alpha j\,|\,\vec{q}\mu)\Delta_{\mu\lambda}(\tilde{\pi}g\cdot\vec{q})\times Q^0_{\vec{q}\lambda}e^{i(\vec{q}\cdot\vec{n}-\omega_{\vec{q}\lambda}t)}+\text{c.c.}\tag{2.26}$$

Actually, due to the block form of $\Delta(g_0,\vec{q})$ only polarization vectors belonging to the same irreducible representation $D^{(\nu)}$ as the chosen $(\vec{q},\lambda)$ mode occur. Therefore if this representation is not one dimensional, the symmetry group of a given $(\vec{q},\lambda)$ mode depends in general on the particular choice of the polarization vector in the corresponding irreducible representation space. Keeping this in mind let us now determine the subgroup U of all translations occurring in G. Accordingly we put in (2.10) $R=1$, $\epsilon=1$. Now any lattice translation $\{1|\vec{n}\}$ of G_0 gives rise to a phase shift $(-\vec{q}\cdot\vec{n})$ in (2.26) which can always be compensated by an appropriate time translation τ satisfying the relation

$$\vec{q}\cdot\vec{n}-\omega_{\vec{q}\lambda}\tau\equiv0\pmod{2\pi}.\tag{2.27}$$

Therefore all $\vec{n}\in\Lambda_3$ occur as spatial components of the elements of U and $\tilde{\pi}U=U_0$. It follows that U is a four-dimensional lattice translation group generated by

$$\begin{aligned}&a_i=(\vec{a}_i,\vec{q}\cdot\vec{a}_i/\omega_{\vec{q}\lambda}),\quad i=1,2,3,\\&a_4=(0,-2\pi/\omega_{\vec{q}\lambda}),\end{aligned}\tag{2.28}$$

where $\vec{a}_1,\vec{a}_2,\vec{a}_3$ generate U_0 and form a basis of Λ_3, whereas the a_ν $(\nu=1,2,3,4)$ form a basis of a four-dimensional lattice denoted by Λ_4. Note that its reciprocal Λ_4^* can be obtained by adding $q\equiv(\vec{q},\omega_{\vec{q}\lambda})$ as a fourth basis vector to the other three $a_i^*=(\vec{a}_i^*,0)$ of Λ_3^* so that we can write

$$\Lambda_4^*=\{\Lambda_3^*,q\}.\tag{2.29}$$

Mutatis mutandis this same translational symmetry was shown to hold in the case of a crystal in the field of an electromagnetic plane wave of four vector $\vec{q}$.[11] Therefore G is a four-dimensional space group, and according to the general theory[12] it is determined by the group of primitive translations U, the point group K, and a set of nonprimitive translations $w(K)$. For mutually degenerate modes the group U is the same.

From (2.13) it follows that $\tilde{\pi}K\subseteq K_0$, where K_0 is the point group of G_0. So we can write $P=(R,\epsilon)\in K$, with R and ϵ satisfying the relation (2.21).

Denoting by K^+ and by $K_{\vec{q}}$ the point groups of G^+ and $G_{\vec{q}}$, respectively, one has with (2.22)

$$\tilde{\pi}K^+\subseteq K_{\vec{q}}.\tag{2.30}$$

If now the mode $(\vec{q}, \lambda)$ belongs to a one-dimensional representation of $G_{\vec{q}}$, then (2.26) becomes

$$[(\tilde{\pi}g)\vec{u}]_\alpha(\vec{n},j)_t = e(\alpha j\,|\,\vec{q}\lambda)Q^0_{\vec{q}\lambda}e^{i[\phi(\tilde{\pi}g)+\vec{q}\cdot\vec{n}-\omega_{\vec{q}\lambda}t]} + \text{c.c.}, \tag{2.31}$$

with $\phi(\tilde{\pi}g)$ real, and there exists always a compensating time translation $\tau_g = \phi(\tilde{\pi}g)/\omega_{\vec{q}\lambda}$ making $g\cdot\vec{u} = \vec{u}$, so that $P = (R, 1)$ belongs to K^+ for all $R \in K_{\vec{q}}$. If now $\vec{w}(R)$ is a nonprimitive translation corresponding to R, so that $\tilde{\pi}g = \{R\,|\,\vec{w}(R)\}$, then that corresponding to P can be chosen as

$$w(P) = (\vec{w}(R), \phi(\tilde{\pi}g)/\omega_{\vec{q}\lambda}). \tag{2.32}$$

If the mode $(\vec{q}, \lambda)$ belongs to an irreducible representation $D^{(\nu)}$ of $G_{\vec{q}}$ of dimension greater than one, then only those elements $g_0 \in G^0_{\vec{q}} \subseteq G_{\vec{q}}$ occur in $\tilde{\pi}G^+$, for which the vectors $e(\alpha j\,|\,\vec{q}\lambda)$, $\alpha = 1, 2, 3$ and $j = 1, 2, \ldots, s$ are eigenvectors of $D^{(\nu)}(g_0)$.

This is equivalent with the condition: g_0 belongs to $G^0_{\vec{q}}$ if and only if

$$\Delta_{\mu\lambda}(g_0, \vec{q})Q^0_{\vec{q}\lambda} = e^{i\phi(g_0)}Q^0_{\vec{q}\mu}, \tag{2.33}$$

and for these elements only, a compensating time translation exists, given as above by (2.32). The elements $g_0 \in U_0$ always satisfy (2.33), so that, as already said, $\tilde{\pi}U = U_0$.

Summarizing the orthochronous space group G^+ is given by

$$\begin{aligned} &U \text{ generated by } a_\nu \ (\nu = 1, \ldots, 4); \\ &K^+ = \{P = (R, 1)\,|\,g_0 = \{R\,|\,\vec{w}(R)\} \in G^0_{\vec{q}}\}, \qquad (2.34) \\ &w(P) = (\vec{w}(R), \phi(g_0)/\omega_{\vec{q}\lambda}). \end{aligned}$$

Let us finally describe briefly the situation for antichronous symmetry elements. If G does not coincide with G^+, the latter is a subgroup of index two. We define a subset $M_{\vec{q}}$ of the space group G_0 by

$$M_{\vec{q}} = \{\{R\,|\,\vec{a}\} \in G_0\,|\,R\vec{q} \equiv -\vec{q} \,(\text{mod } \Lambda_3^*)\}. \tag{2.35}$$

If $\vec{q} \not\equiv -\vec{q}$ (mod Λ_3^*), the unitary representation $\Gamma_{\vec{q}}$ of $G_{\vec{q}}$ induces a $6s$-dimensional corepresentation $\Gamma^{\text{co}}_{\vec{q}}$ of the group $G^{\text{co}}_{\vec{q}} = \{G_{\vec{q}}, M_{\vec{q}}\}$, where now $M_{\vec{q}}$ forms the coset of $G^{\text{co}}_{\vec{q}}$ represented by the antiunitary operators.

If $\vec{q} \equiv -\vec{q}$ (mod Λ_3^*), then $M_{\vec{q}} = G_{\vec{q}}$ and $\Gamma_{\vec{q}}$ induces a $3s$-dimensional corepresentation of $G_{\vec{q}} \times C_2$ also denoted by $\Gamma^{\text{co}}_{\vec{q}}$. In both cases the irreducible components of the corepresentation $\Gamma^{\text{co}}_{\vec{q}}$ characterize the different branches of normal modes. Again the elements $g_0 \in G^{\text{co}}_{\vec{q}}$, and only those, for which the polarization vectors $e(\alpha j\,|\,\vec{q}\lambda)$ of the mode $(\vec{q}, \lambda)$ are eigenvectors, admit a compensating time translation τ_g, with $\tilde{\pi}g = g_0$ and occur thus as spatial part of the elements of G. The procedure for finding K and $w(K)$ is the same as above.

The essential results obtained so far can be formulated in following proposition:

Proposition 1: The symmetry group of a vibrating harmonic crystal in the single-mode approximation is a four-dimensional crystallographic space-time group G, which is a (3, 1) reducible subgroup of the inhomogeneous Galilei group IG(4). The components of G acting on the space only form a three-dimensional space group $\tilde{\pi}G$ which is an equitranslational subgroup of G_0, the symmetry group of the basic structure.

If several normal modes become relevant, then the space-time symmetry of the crystal vibrating according to the superposition of these normal modes will, in general, be lowered. Its symmetry will only be described by a four-dimensional space group if the basisvectors of Λ_3^* and the relevant wave vectors $(\vec{q}, \omega_{\vec{q}\lambda})$ span a four-dimensional lattice. This is, e.g., the case if these vectors are of the special form $q_z = (z\vec{q}_0, z\omega_{\vec{q}_0\lambda})$ for $z \in Z$ (Z being the ring of integers). This case is expected to occur only if the relevant dispersion relation is a linear one.

In Appendixes B and C one can find the groups G that can occur for a crystal of the Na_2CO_3 type ($G_0 = C2/m$) vibrating in a single mode.

III. PERIODIC STATIC DISTORTIONS

As in Sec. II, a periodic lattice distortion is considered of a basic structure described by a point mass distribution X_0 having a three-dimensional space group G_0 as symmetry. The set of atomic positions $\{\vec{r}(\vec{n},j)\}$ in the distorted crystal is given by a displacement vector field $\vec{u}$ defined by

$$\vec{r}(\vec{n},j) = \vec{r}_0(\vec{n},j) + \vec{u}(\vec{n},j), \tag{3.1}$$

with $\vec{r}_0(\vec{n},j)$ as in (2.1), and $\vec{u}$ a periodic vector field

$$\vec{u}(\vec{n},j) = \sum_{\substack{\vec{q}\in D_d^* \\ \vec{q}\in BZ(\Lambda_3^*),\, \vec{q}\neq 0}} \vec{f}_j(\vec{q})e^{i\vec{q}\cdot\vec{n}}, \tag{3.2}$$

with D_d^* a d-dimensional lattice ($d \leqslant 3$), and $\vec{q}$ restricted to the first Brillouin zone of Λ_3^*. The mass distribution is

$$X = \sum_{\vec{n}j} m_j\delta(\vec{r} - \vec{r}(\vec{n},j)).$$

One is interested in the relations between the diffraction pattern and the atom distribution X. One can of course in principle calculate directly such a pattern, which amounts to the evaluation of the Fourier transform of X. The point is that due to the periodicity of $\vec{u}$ one gets extinctions that do not follow from the Euclidean symmetry of X, which in general can be very low. This is in particular the case when D_d^* is three-dimensional and completely incommensurable with respect to Λ_3^* (i.e., if $D_d^* \cap \Lambda_3^* = 0$). Therefore in addition to the rigid Euclidean transformations of X as a whole, one also considers relative motions of the periodic distortion with respect to the basic crystal.

So that instead of (3.2) we put

$$\vec{u}(\vec{n},j)_{\vec{t}}=\sum_{\vec{q}\in D_d^*}\vec{f}_j(\vec{q})e^{i\vec{q}\cdot(\vec{n}-\vec{t})} \tag{3.3}$$

(where it is sufficient to take for $\vec{t}$ arbitrary vectors in the d-dimensional space spanned by D_d), and also

$$\vec{r}(\vec{n},j)_{\vec{t}}=\vec{r}_0(\vec{n},j)+\vec{u}(\vec{n},j)_{\vec{t}}. \tag{3.4}$$

We introduce

$$X_{\vec{t}}=\sum_{\vec{n}j}m_j\delta(\vec{r}-\vec{r}(\vec{n},j)_{\vec{t}})$$

as a generalization of X_0. Looking at the symmetries of $X_{\vec{t}}$ (and those of X as a special case) it is natural to extend the admitted transformations, adding to the "external" three-dimensional Euclidean ones in V_3 the "internal" d-dimensional relative motions in V_d. Considering V_d as subspace of V_3 the latter are not Euclidean: they can be made Euclidean by treating V_d as a Euclidean space V_d different from V_3, by imbedding $X_{\vec{t}}$ into the product space $V_3\oplus V_d$. This imbedding denoted by $\tilde{X}$ is not unique. A natural one which is a generalization of that considered in Sec. II is given by

$$l:\vec{r}(\vec{n},j)_{\vec{t}}\to(\vec{r}(\vec{n},j)_{\vec{t}},\vec{t}). \tag{3.5}$$

The admitted transformations are accordingly extended from E(3) to the direct product group E(3) × E(d). The transformation law for an element $(\vec{x},\vec{y})\in V_3\oplus V_d$ by $g=(g_E,g_I)\in \mathrm{E}(3)\times\mathrm{E}(d)$ [with $g_E\in\mathrm{E}(3)$ and $g_I\in\mathrm{E}(d)$, where g_E and g_I represent the "external" and "internal" part, respectively, of g] is given by

$$\begin{aligned}(g_E,g_I)(\vec{x},\vec{y})&\equiv(g_E\vec{x},g_I\vec{y})\\&=(R_E\vec{x}+\vec{a}_E,R_I\vec{y}+\vec{a}_I).\end{aligned} \tag{3.6}$$

In this way the symmetry group of $\tilde{X}$ is defined as

$$G=\{g\in\mathrm{E}(3)\times\mathrm{E}(d)\,|\,g\tilde{X}=\tilde{X}\}. \tag{3.7}$$

Lemma 2: If $g\tilde{X}=\tilde{X}$, then $(\tilde{\pi}g)X_0=X_0$.

Proof: Introduce the average of $\vec{r}(\vec{n},j)_{\vec{t}}$ over a unit cell of D_d of volume V:

$$\langle\vec{r}(\vec{n},j)_{\vec{t}}\rangle\equiv\frac{1}{V}\int d\vec{t}\,\vec{r}(\vec{n},j)_{\vec{t}}=\vec{n}+\vec{r}_j, \tag{3.8}$$

because $\vec{q}=0$ does not appear in the spectrum of $\vec{u}(\vec{n},j)$. Consider g such that $g\tilde{X}=\tilde{X}$. Then

$$\begin{aligned}(\tilde{\pi}g)(\vec{n}+\vec{r}_j)=(\tilde{\pi}g)\langle\vec{r}(\vec{n},j)_{\vec{t}}\rangle&=\{R_E\,|\,\vec{a}_E\}\langle\vec{r}(\vec{n},j)_{\vec{t}}\rangle\\&=\langle\vec{r}(\vec{n}',j')_{\vec{t}'}\rangle=\vec{n}'+\vec{r}_{j'},\end{aligned} \tag{3.9}$$

because the invariance of $\tilde{X}$ can be expressed more explicitly by

$$\begin{aligned}g(\vec{r}(\vec{n},j)_{\vec{t}},\vec{t})&=(R_E\vec{r}(\vec{n},j)_{\vec{t}}+\vec{a}_E,R_I\vec{t}+\vec{a}_I)\\&=(\vec{r}(\vec{n}',j')_{\vec{t}'},\vec{t}').\end{aligned} \tag{3.10}$$

This proves the lemma. Hence

$$\tilde{\pi}G\subseteq G_0. \tag{3.11}$$

The relation in Eq. (3.10) between primed and unprimed variables is given as follows:

$$\begin{aligned}&R_E\vec{r}_j+\vec{a}_E=\vec{r}_{j'}+\vec{u}(g_E,j),\\&R_E\vec{n}=\vec{n}'-\vec{u}(g_E,j),\end{aligned} \tag{3.12}$$

and the invariance of the displacement vector field is expressed as

$$\begin{aligned}&R_E\vec{u}(\vec{n},j)_{\vec{t}}=\vec{u}(\vec{n}',j')_{\vec{t}'},\\&\vec{t}'=R_I\vec{t}+\vec{a}_I.\end{aligned} \tag{3.13}$$

To find the elements of G_0 occurring in $\tilde{\pi}G$ we consider the transformation of the displacement field (3.3): $g=(g_E,g_I)\in G$ if and only if $g_E\in G_0$ and

$$R_ES\subseteq S, \tag{3.14}$$

where S is the spectrum of $\vec{u}$,

$$R_I\vec{q}=R_E\vec{q},\ \vec{q}\in S, \tag{3.15}$$

$$R_E\vec{f}_j(R_E^{-1}\vec{q})=\vec{f}_{j'}(\vec{q})e^{i\vec{q}\cdot[\vec{u}(g_E,j)-\vec{a}_I]}. \tag{3.16}$$

In this way we can easily determine the translation elements of G. If we identify $\vec{m}$ and $\{1|\vec{m}\}$ for $\vec{m}\in U_0$, it follows from (3.12) that $\vec{u}(\vec{m},j)=\vec{m}$ for all j. Hence $(\vec{m},\vec{a}_I)\in G$ if $\vec{q}\cdot\vec{a}_I\equiv\vec{q}\cdot\vec{m}\ (\mathrm{mod}\ 2\pi)$. Denoting the projection of $\vec{m}$ on V_d (considered as subspace of V_3) by $\Delta\vec{m}$, one has

$$(\vec{m},\Delta\vec{m})\in G,\quad \vec{m}\in U_0. \tag{3.17}$$

Furthermore, because of the periodicity of the distortion $\vec{u}$,

$$(0,\vec{d})\in G,\quad \vec{d}\in D_d \tag{3.18}$$

follows from Eq. (3.16). All these translations form a group U generated freely by a basis of a $(3+d)$-dimensional lattice Σ_{3+d} in $V_3\oplus V_d$. If $\{\vec{a}_j, j=1,2,3\}$ forms a basis of Λ_3 and $\{\vec{b}_l, l=1,\ldots,d\}$, one of D_d one has

$$\begin{aligned}G\supseteq U=\{(\vec{a}_j,\Delta\vec{a}_j),\,(0,\vec{b}_l),\ &j=1,2,3;\\ &l=1,\ldots,d\}\cong Z^{3+d}.\end{aligned} \tag{3.19}$$

The point-group elements are $R=(R_E,R_I)$ and the set of nonprimitive translations follows from Eq. (3.16). The distribution $X_{\vec{t}}$ is defined for all $\vec{t}\in V_d$. One can also generate a distribution $\tilde{X}$ in $V_3\oplus V_d$ by the action of G on X_0, because U spans $V_3\oplus V_d$. However, in this case the positions in the unit cell of Σ_{3+d} are, in general, discrete. Let us consider now the positions taken by the atom j of X_0. From Eq. (3.3) we get the relation

$$\vec{u}(\vec{n},j)_0=\vec{u}(\vec{0},j)_{-\Delta\vec{n}}, \tag{3.20}$$

from which we deduce, that for each j there corresponds as many different positions as the cardinality of equivalence classes of the relation in Λ_3:

$$\vec{n}\sim\vec{n}' \text{ if and only if } \Delta\vec{n}\equiv\Delta\vec{n}' \pmod{D_d}. \tag{3.21}$$

If $\Lambda_3\cap D_d$ is a d-dimensional lattice, then Λ_3 and D_d are called commensurable. The restriction $\Lambda_3\cap V_d$ is a lattice containing D_d as a sublattice of finite index s':

$$D_d\subseteq(\Lambda_3\cap V_d),\quad (\Lambda_3\cap V_d):D_d=s'. \tag{3.22}$$

If $\Lambda_3\cap D_d$ is not d-dimensional, then Λ_3 and D_d are called incommensurable and the number s' of classes with respect to relation (3.21) is infinite.

This increase from s to ss' particles per unit cell in going from Λ_3 to $\tilde{\Sigma}_{3+d}$ does not depend on the product-space description adopted here. In fact, looking at the (external) Euclidean symmetry only, the unit cell (in V_3) of a periodically distorted lattice is s' times larger than that of the basic lattice Λ_3. This situation is not changed if in addition one considers elements $g\in G$ for which $\tilde{\pi}g\in G_0$. No new different positions arise, they only get possibly equivalent. However, since now we consider a set of points in $V_3\oplus V_d$, Lemma 2 can no longer be used. Possibly there are elements g of $\mathrm{E}(3)\times\mathrm{E}(d)$, or even of $\mathrm{E}(3+d)$, which have not the property $\tilde{\pi}g\in G_0$ or for which $\tilde{\pi}g$ is even not defined. This situation may occur only if special correlations exist between the positions $\vec{r}_j$ in X_0 and the distortion $\vec{u}$. The additional symmetry elements may be considered as accidental. Although they are interesting, we shall not discuss them here. So we have:

Proposition 2: Disregarding accidental symmetries, the symmetry group G of a periodically distorted crystal is a $(3+d)$-dimensional space group, and a subgroup of $\mathrm{E}(3)\times\mathrm{E}(d)$. The external space components of G form a three-dimensional space group $\tilde{\pi}G$, which is an equitranslational subgroup of G_0, the space group of the basic structure.

This proposition recalls that of Sec. II. The difference is that there $\tilde{X}$ describes a discrete set of continuous lines, here (in general) a discrete set of points. Furthermore in Sec. II the metric relation between the (external) space and the time space is given by a dispersion law, here by the fact that different motions are considered in the same Euclidean space.

To make the link more explicit, let us consider a crystal vibrating according to the single mode $(\vec{q},\omega_{\vec{q}\lambda})$. At any fixed time $t=t_0$ its symmetry can be analyzed according to the present section for the case $d=1$. One then gets for the $\Delta\vec{a}_i$ and the $\vec{b}_j$ appearing in (3.19) ($i=1,2,3$ and $j=1$)

$$\Delta\vec{a}_i=(\vec{q}\vec{a}_i/|\vec{q}|^2)\vec{q},\quad \vec{b}_1=-(2\pi/|\vec{q}|^2)\vec{q}. \tag{3.23}$$

Identification of V_1 with the space spanned by the time and comparison with (2.28) shows that the group U (and G also) is the same as in the time-dependent case if the metric relation between V_3 and V_1 is that given by

$$\omega_{\vec{q}\lambda}=|\vec{q}|, \tag{3.24}$$

which corresponds to choose units such that the phase velocity becomes $v_{\vec{q}\lambda}=1$. The restriction mentioned at the end of Sec. II implies that this still can be done even if several $\vec{q}$'s occur. As in Sec. II one can, here also, apply the results of the representation theory of G_0, based now on the transformation properties of $\vec{u}(\vec{n},j)_{\vec{t}}$ under G_0. We do not want here to go into more details. An example can be found in Appendixes C and D, where the case of Na_2CO_3 in the modulated phase is treated. Before showing that it is indeed possible to derive extinction rules for diffraction from symmetry elements of the product space, which is one of the main justifications for the present approach, it is convenient to treat first a more general model for the crystal than that in terms of point atoms only.

IV. STATIC DENSITY DISTORTIONS

In this section we consider a crystal described in terms of a density function $\rho=\rho(\vec{r})$, defined on a three-dimensional Euclidean space V_3, that admits a Fourier decomposition

$$\hat{\rho}(\vec{k})=\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}\rho(\vec{r}), \tag{4.1}$$

then $\hat{\rho}$, the Fourier transform of ρ, is a function on the dual space V_3^*. We denote by the spectrum S of ρ the support of $\hat{\rho}$

$$S=\{\vec{k}\in V_3^*\,|\,\hat{\rho}(\vec{k})\neq 0\}.$$

The elements of S give rise, in the geometrical approximation of a diffraction experiment on the crystal, to the well-known Bragg reflections. We now suppose, as discussed in Sec. I, that one can distinguish between "main reflections" (belonging to S_m) and "satellite reflections" (belonging to S_s) and that there is a unique decomposition

$$S=S_m+S_s, \tag{4.2}$$

such that: (i) the main reflections generate a three-dimensional lattice Λ_3^*

$$\Lambda_3^*=\{S_m\}; \tag{4.3}$$

(ii) the satellite reflections generate, modulo Λ_3^*, a

d-dimensional lattice $(1 \leqslant d \leqslant 3)$ D_d^*

$$D_d^* = \{S_s(\text{mod } \Lambda_3^*)\}; \qquad (4.4)$$

(iii) reflections belonging to a given fixed lattice D_d^* are satellite of a uniquely determined main reflection. This last condition is satisfied in the case that

$$\Lambda_3^* \cap D_d^* = 0, \qquad (4.5)$$

which implies that D_d^* and Λ_3^* are incommensurable, and is not true for superstructures because these arise from a commensurate deformation.

Strictly speaking, and because of the presence of the experimental error, it is not possible to decide whether satellite reflections are commensurate or not with the main reflections. Therefore condition (iii), as well as the uniqueness of the decomposition (4.2) deserve some comments.

In the case of a superstructure Λ_3^* and D_d^* generate a three-dimensional lattice Σ_3^*

$$\{\Lambda_3^*, D_d^*\} = \Sigma_3^*, \qquad (4.6)$$

implying $S \subseteq \Sigma_3^*$. Therefore the symmetry group of ρ is a three-dimensional space group. For Σ_3^* to be physically relevant one actually also requires that the change of Σ_3^* as a function of the temperature, in a given finite temperature interval outside the phase transition point, is continuous. Thus

$$\lim_{\Delta T \to 0} [\Sigma_3^*(T + \Delta T) - \Sigma_3^*(T)] = 0 \quad \text{for } T_1 < T < T_2. \qquad (4.7)$$

This last condition implies that D_d^* and Λ_3^* scale in the same way as a function of T.

It was precisely because of the experimental evidence of cases in which the variation of D_d^* with temperature was different from that of Λ_3^*, that the concept of modulated crystal[4] has been introduced, for which Eqs. (4.6) and (4.7) are not both satisfied. Therefore either Σ_3^* does not exist or is not physically relevant, and the symmetry of such a crystal is not properly described by the Euclidean symmetry elements of V_3 only. This because there are crystals with infinite fundamental cell having a region of coherent scattering as big as in crystals with a finite fundamental cell. So that the correlation function between two atoms in the structure is in both cases (at least in principle) of infinite range. In the case of a modulated crystal this ordering of many atoms in the same fundamental cell often gives rise to systematic extinctions not due to space-group symmetries, a situation shared by long-period superstructures. But even in modulated structures (for $d \geqslant 1$) condition (iii) needs not to be true. The point is that, strictly speaking, the satellites commensurable with the main reflections can always be included in a new defined set S_m' of main reflections, such that the new subdivision $S = S_m' + S_s'$ satisfies the above conditions. From a practical point of view, however, even in the case of superstructures (the long-period ones in particular) ambiguity in labeling the vectors $\vec{k}$ is present only with reflections giving a negligible contribution to the structure determination. Here, and from now on, we assume that conditions (4.2)–(4.5) are satisfied for the relevant reflections at least.

It then follows that any element $\vec{k}$ of S can be written uniquely as a linear combination with integral coefficients of three linearly independent main reflection vectors $\vec{a}_i^*$ $(i = 1, 2, 3)$ generating Λ_3^*, and d linearly independent satellite reflections $\vec{b}_j^*$ generating D_d^*:

$$\vec{k} = \sum_{i=1}^{3} z_i \vec{a}_i^* + \sum_{j=1}^{d} z_{3+j} \vec{b}_j^*, \quad z_l \in Z, \qquad (4.8)$$

so that $\vec{k} = \vec{k}'$ implies $z_l = z_l'$, $l = 1, \ldots, 3+d$. One can assume without restriction that

$$\vec{b}_i^* \in BZ, \quad i = 1, \ldots, d, \qquad (4.9)$$

where BZ denotes the (first) Brillouin zone defined by Λ_3^*. In this case the $\vec{b}_j^*$ are called basic satellite reflection vectors.

We are now able to imbed the spectrum S into a $(3+d)$-dimensional reciprocal space $V_3^* \oplus V_d^*$, interpreted as reciprocal of the direct sum of the external space V_3, and the internal one V_d. The imbedding is not unique, but there is a natural one, compatible with that considered in (3.5).

In the reciprocal space the spectrum S is imbedded linearly into $\tilde{S} \subset V_3^* \oplus V_d^*$ in such a way that

$$\pi_* \tilde{S} = S, \qquad (4.10)$$

when π_* is the projection: $V_3^* \oplus V_d^* \to V_3^*$. Since relation (4.8) is 1 to 1, we know the imbedding of $\vec{k} \in S$, as soon as that of $\vec{a}_i^*$ and $\vec{b}_j^*$ is given. The $\vec{a}_i^*$ being associated with translational symmetry in the external space V_3, they have a vanishing internal component

$$l_*: \ \vec{a}_i^* \to a_i^* \equiv (\vec{a}_i^*, 0), \quad i = 1, 2, 3. \qquad (4.11)$$

The $\vec{b}_j^*$ are associated with the periodicity in the internal space V_d, so that their internal component has to be $\vec{b}_j^*$. Since they occur also in S, according to (4.10) their external component is also $\vec{b}_j^*$:

$$l_*: \vec{b}_j^* \to a_{j+3}^* \equiv (\vec{b}_j^*, \vec{b}_j^*), \quad j = 1, \ldots, d. \qquad (4.12)$$

For $\vec{k} \in S$ as in (4.8) one has

$$l_*: \vec{k} \to k = (\vec{k}, \Delta\vec{k}) = \sum_{\nu=1}^{3+d} z_\nu a_\nu^*. \qquad (4.13)$$

We extend the improduct defined in V_3 and in V_d to one in $V_3 \oplus V_d$ by

$$(\vec{a}, \vec{b}) \cdot (\vec{k}, \vec{l}) \equiv \vec{a}\vec{k} - \vec{b}\vec{l}. \qquad (4.14)$$

This gives a natural isomorphism between $V_3^* \oplus V_d^*$ and $V_3 \oplus V_d$. Then l_* induces a mapping l from functions on V_3 to functions on $V_3 \oplus V_d$: $l\rho = \tilde{\rho}$, where

$$\tilde{\rho}(\vec{r}, \vec{t}) = \sum_{\vec{k} \in S} \hat{\rho}(\vec{k}) e^{i(l_* \vec{k}) \cdot (\vec{r}, \vec{t})} \tag{4.15}$$

or

$$\tilde{\rho}(r) = \sum_{k \in \tilde{S}} \hat{\rho}(k) e^{ikr}. \tag{4.16}$$

The action of $g = (g_E, g_I) \in \mathbf{E}(3) \times \mathbf{E}(d)$ on the scalar function $\tilde{\rho}$ is the standard one

$$(g\tilde{\rho})(r) \equiv \rho(g^{-1} r)$$

or (4.17)

$$[(g_E, g_I)\tilde{\rho}](\vec{r}, \vec{t}) = \tilde{\rho}(g_E^{-1} \vec{r}, g_I^{-1} \vec{t}).$$

The symmetry group G of the imbedded $\tilde{\rho}$ is now well defined:

$$G = \{ g \in \mathbf{E}(3) \times \mathbf{E}(d) \,|\, g\tilde{\rho} = \tilde{\rho} \}. \tag{4.18}$$

One now easily verifies that $\tilde{\rho}$ is left invariant by the $(3+d)$ linearly independent translations a_ν which form a basis in $V_3 \oplus V_d$ reciprocal to that given by the a_ν^* of (4.11) and (4.12). One finds

$$\begin{aligned} a_i &= (\vec{a}_i, \Delta\vec{a}_i), \quad i = 1, 2, 3, \\ a_{3+j} &= (0, -\vec{b}_j), \quad j = 1, \ldots, d, \end{aligned} \tag{4.19}$$

where as in Sec. III, $\Delta\vec{a}_i$ is the projection of $\vec{a}_i$ on V_d (considered as subspace of V_3). We are back to (3.19) up to a sign due to the definition of reciprocal basis. Again these are not the only possible symmetry translations, but the additional ones can be considered accidental, in the sense that they do not follow from the existence of Λ_3^* and D_d^* only.

Disregarding accidental symmetries, the subgroup U of G of all translations is freely generated by the basis $\{a_1, \ldots, a_{3+d}\}$ and

$$U \cong Z^{3+d}. \tag{4.20}$$

As U generates in $V_3 \oplus V_d$ a $(3+d)$-dimensional lattice Σ_{3+d} the group G is a $(3+d)$-dimensional space group.

Writing now a general element $g \in G$ as

$$g = (\{R_E | \vec{a}_E\}, \{R_I | \vec{a}_I\}),$$

the symmetry condition (4.18) implies for the Fourier component $\hat{\rho}(\vec{k})$ because of (4.16),

$$R_E S \subseteq S, \tag{4.21}$$

$$\hat{\rho}(R_E \vec{k}) = \hat{\rho}(\vec{k}) e^{-i[(R_E \vec{k}) \cdot \vec{a}_E - (R_I \Delta\vec{k}) \cdot \vec{a}_I]}, \tag{4.22}$$

$$\begin{aligned} &\Delta(R_E \vec{k}) = R_I(\Delta\vec{k}) \quad \text{for all } \vec{k} \in S, \\ &\Delta(R_E \vec{a}) \equiv R_I(\Delta\vec{a}) \pmod{D_d} \quad \text{for all } \vec{a} \in \Lambda_3. \end{aligned} \tag{4.23}$$

For main reflections $\Delta\vec{k} = 0$, according to (4.11), and only for those. This implies by (4.23) the condition

$$R_E S_m \subseteq S_m \tag{4.24}$$

and, because S_m generates Λ_3^*, also

$$R_E \Lambda_3^* = \Lambda_3^*. \tag{4.25}$$

It is therefore convenient to consider the so called "average structure" associated with the density function ρ_m obtained by taking into account the main reflections only

$$\rho_m(\vec{r}) \equiv \sum_{\vec{k} \in S_m} \hat{\rho}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} = \sum_{\vec{n} \in \Lambda_3} \rho(\vec{r} - \vec{n}). \tag{4.26}$$

This last equation explains the name average structure.

Because of (4.26) the symmetry of ρ_m is a three-dimensional space group G_m. Considering again the projection $\tilde{\pi}$: $\mathrm{E}(3) \times \mathrm{E}(d) \to E(3)$, one directly verifies that in $\tilde{\pi}G$ all those elements of G_m occur for which a compensating internal transformation g_I can be found satisfying (4.22) and (4.23). This is in particular the case for the elements of U, so that $\tilde{\pi}G$ appears to be a three-dimensional space group, which is an equitranslational subgroup of G_m. These results can be summarized in the following proposition:

Proposition 3: Disregarding accidental symmetries, the symmetry group of the density function describing a periodically distorted crystal is a $(3+d)$-dimensional space group G. The components of the elements of G that act on the external space form a three-dimensional space group $\tilde{\pi}G$, which is an equitranslational subgroup of G_m, the symmetry group of the average crystal structure.

The only difference with proposition 2 is that here the symmetry group G_m of the average structure appears instead of G_0 of the basic structure. As the case described in Sec. III is a special case of the present one, proposition 2 remains true if one replaces there G_0 by G_m and thus by $G_m \cap G_0$ also, which is again a three-dimensional space group having the same lattice translations. Besides this property, the mutual relations between G_m and G_0 are not easily characterized.

For sufficiently small deformations, and in a point-atom description, we show in Appendix E, that G_m is a subgroup of G_0. There, the connection between deformed, basic and average structure is explicitly given.

For the determination of G for a given structure, the following lemma can be useful.

Lemma 3: Suppose $(\{R_E | \vec{a}_E\}, \{R_I | \vec{a}_I\}) \in G$. Then the point-group components satisfy the relation

$$R_E \vec{b}_j^* \equiv R_I \vec{b}_j^* \pmod{\Lambda_3^*}, \tag{4.27}$$

where $\vec{b}_j^*$ represents basic satellite reflections.

Proof: Use (4.8), (4.12), and (4.23). Notice that (2.21) is a particular case of (4.27).

We are now able to discuss briefly the extinctions due to the elements of G. There are two types of extinctions: those due to nonprimitive lattices, and those due to nonprimitive translations.[13]

A. Extinctions due to nonprimitive lattices

1. Product space notation

Equation (4.16) can be written

$$\tilde{\rho}(r) = \sum_{k \in \tilde{\Sigma}^*_{3+d}} \hat{\rho}(k) e^{ikr},$$

with $\tilde{\Sigma}_{3+d}$ generated by the a_ν of (4.19). Any corresponding nonprimitive lattice $\tilde{\Gamma}_{3+d}$ gives rise to the relations

$$\tilde{\Gamma}_{3+d} \subset \tilde{\Sigma}_{3+d} \quad \text{thus} \quad \tilde{\Sigma}^*_{3+d} \subset \Gamma^*_{3+d}.$$

Writing

$$\tilde{\rho}(r) = \sum_{k \in \tilde{\Gamma}^*_{3+d}} \hat{\rho}(k) e^{ikr},$$

one gets the extinction rule

$$\hat{\rho}(k) = 0 \quad \text{for all } k \in \tilde{\Gamma}^*_{3+d} \text{ but } k \notin \tilde{\Sigma}^*_{3+d}. \tag{4.28}$$

2. Three-dimensional Euclidean space notation

Consider the projection π_*: $k = (\vec{k}, \Delta\vec{k}) \to \vec{k}$. Then it follows that $S \subset \pi_* \Sigma^*_{3+d}$; because $\hat{\rho}(k) = \hat{\rho}(\vec{k})$ one has

$$\rho(\vec{r}) = \sum_{\vec{k} \in \pi_* \tilde{\Gamma}^*_{3+d}} \hat{\rho}(\vec{k}) e^{i\vec{k}\cdot\vec{r}},$$

giving the extinction rule

$$\hat{\rho}(\vec{k}) = 0 \quad \text{for all } \vec{k} \in \pi_* \tilde{\Gamma}^*_{3+d} \text{ but } \vec{k} \notin \pi_* \tilde{\Sigma}^*_{3+d}. \tag{4.29}$$

As the mapping $l_* \vec{k} = k$ is 1 to 1, (4.29) is equivalent with (4.28).

B. Extinctions due to nonprimitive translations

1. Product-space notation

The invariance of $\tilde{\rho}$ with respect to $g = \{R \,|\, n + w(R)\} \in G$ where $n \in U$ and $w(R) \notin U$, for $w(R) \neq 0$, implies

$$\hat{\rho}(Rk) = \hat{\rho}(k) e^{-i(Rk)\cdot w(R)}. \tag{4.30}$$

This condition gives rise to the following extinction rules:

$$Rk = k \quad \text{and} \quad k \cdot w(R) \not\equiv 0 \pmod{2\pi} \tag{4.31}$$

implies $\hat{\rho}(k) = 0$.

2. Three-dimensional Euclidean space notation

Denote g as above by $g = (g_E, g_I)$; $R = R_E \oplus R_I$ and $w(R) = (\vec{w}(R_E), \vec{v}(R_I))$, $g_E = \{R_E \,|\, \vec{n} + \vec{w}(R_E)\}$, $g_I = \{R_I \,|\, \Delta\vec{n} + \vec{v}(R_I)\}$, $g = \{R \,|\, n + w(R)\}$. Then from (4.22) one gets the extinction rule

$$R_E \vec{k} = \vec{k} \quad \text{and} \quad \vec{k} \cdot \vec{w}(R_E) - \Delta\vec{k} \cdot \vec{v}(R_I) \not\equiv 0 \pmod{2\pi}$$

implies

$$\hat{\rho}(\vec{k}) = 0. \tag{4.32}$$

But (4.31) is equivalent with (4.32). Indeed $Rk = k$ implies $R_E \vec{k} = \vec{k}$.

Conversely: from $R_E \vec{k} = \vec{k}$ follows by (4.23) also $Rk = k$. The phase condition is then the same.

Concluding this section we see that indeed systematic extinctions for $\rho(\vec{r})$ are interpretable as space-group extinctions of $\tilde{\rho}(r)$, not necessarily given by Euclidean symmetry properties of $\rho(\vec{r})$, as already recognized by de Wolff[2] (and by La Fleur as mentioned in the same reference).

V. TIME-DEPENDENT DENSITY DISTORTIONS

Considered here is a crystal described by a time-dependent density function $\tilde{\rho}(\vec{r}, t)$ which is (i) periodic in time

$$\tilde{\rho}(\vec{r}, t + T) = \tilde{\rho}(\vec{r}, t), \tag{5.1}$$

with $\Omega = 2\pi/T \ll 10^{18}$ Hz, a typical x-ray frequency;

(ii) periodically distorted at any given time t. (5.2)

A vibrating crystal in the single $\vec{q}$-mode approximation satisfies the above conditions and $\Omega = \omega_{\vec{q},\lambda}$ (see Sec. II), and we restrict here also our considerations to this single-mode case. Then $\tilde{\rho}(\vec{r}, t)$ admits a Fourier decomposition

$$\tilde{\rho}(r) = \sum_{k \in \tilde{S}} \hat{l}(k) e^{ik\cdot r}, \tag{5.3}$$

where we used the notation $r = (\vec{r}, t) \in V_3 \oplus V_1$; $k = (\vec{k}, \omega) \in V_3^* \oplus V_1^*$ and $k \cdot r = \vec{k} \cdot \vec{r} - \omega t \in R$. Because of the assumptions made, the x-ray scattering is determined by the instant density distribution $\rho(\vec{r}) = \tilde{\rho}(\vec{r}, t_0)$, for fixed t_0. Because of Eq. (5.2) and on the basis of the results of the previous section, a natural subdivision occurs in main reflections S_m and satellite reflections S_s in the projected spectrum

$$S \equiv \pi_* \tilde{S} = S_m + S_s, \tag{5.4}$$

with π_* defined as above, and where S_m and S_s satisfy Eqs. (4.3) and (4.4), respectively, for $d = 1$. This subdivision corresponds to that one observes in the Bragg diffraction spots.

The imbedding of $\rho(\vec{r})$ into the space time is here already given $l\rho(\vec{r}) = \tilde{\rho}(\vec{r}, t)$. The corresponding imbedding in the reciprocal space giving $\tilde{S} = l_* S$

needs some care. The dispersion relation $\vec{k}=\vec{k}(\omega)$ fixes the imbedding $l_*\vec{k}=(\vec{k},\omega)$ for the vector $\vec{q}$ of the single mode only according to the relation

$$q=l_*\vec{q}=(\vec{q},\omega_{\vec{q}\lambda}),\quad \vec{q}\in \mathrm{BZ}\text{ of }\Lambda_3^*, \tag{5.5}$$

but not for all other satellite reflections. Note that a single $\vec{q}$ appearing in the distortion [like in Eq. (2.18)] does not mean that it is the only one appearing in S_s (see Appendix E). However, D_1^* is generated by $\vec{q}$, so that it can be taken as the basic satellite, and this fixes the imbedding l_*.

Writing a general element of S as

$$\vec{k}=\sum_{i=1}^{3} z_i\,\vec{a}_i^{\,*}+z_4\vec{q},\quad z_l\in Z,\ l=1,2,3,4,$$

the imbedding l_* is defined by

$$k=l_*\vec{k}=(\vec{k},z_4\omega_{\vec{q},\lambda}), \tag{5.6}$$

which is exactly what one finds on the basis of a point-atom approximation of a vibrating crystal.

Once this step is done, one can apply straightforwardly the results of the previous section for finding the symmetry of $\rho(r)$. The only difference is that here the internal space can be identified with that of the time (after the choice of the natural unit $v=\omega_{\vec{q}\lambda}/|\vec{q}|=1$.) Again the question arises, whether or not in this time-dependent case non-(3, 1)-reducible symmetry elements can occur. These transformations should also leave the underlying space-time structure invariant and thus be nontrivial Galilei (or Lorentz) transformations. As we have seen in Sec. II, such transformations do not leave a simple world line pattern invariant. With $\rho(\vec{r})$ more general patterns are possible, and then additional symmetry elements are possible, in principle at least.

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APPENDIX A: EXAMPLES OF MODULATED CRYSTALS

The occurrence of commensurable distortions in crystals giving rise to superstructures is a very common phenomenon. Also well known is the case of magnetic structures incommensurable with the periodicity of the crystal lattice. But it is only in recent years, that one became increasingly aware of the existence of solid state systems with long-range order without three-dimensional lattice periodicity. Since general attention has been focused on CDW's and on SDW's one has realized, that the number of such systems could be fairly large and was not restricted to CDW and SDW phenomena only. Without trying to be exhaustive, a member of concrete examples of crystals showing incommensurable periodic phenomena (modulation) are indicated in Table I.

TABLE I. Examples of modulated crystals. (PTZ: phenothiazine; TCNQ: tetracyanoquinodimethane; TTF: tetrathiafulvalene; TMTTF: tetramethyltetrathiafulvalene; CuAu II: modification of superlattice near the stoichiometric composition CuAu stable between 380 °C and 410 °C.)

Ionic crystals with displacive modulation	
	γ-Na_2CO_3 (Refs. 4, 15), K_2MoO_4 (Refs. 15, 16), Rb_2WO_4 (Refs. 15, 16), Rb_2ZnCl_4, Rb_2ZnBr_4 (in general, A_2ZnX_4) (Ref. 17), KO_2 (Ref. 18), $NaNO_2$ (Ref. 19), $SC(NH_2)_2$ (thiourea) (Ref. 20), $FeSi\cdot 6H_2O$, $MgSiF_6\cdot 6H_2O$, $MnSiF_6\cdot 6H_2O$ (Ref. 21), $Mn_{15}Si_{26}$(?) (Ref. 22), $Ba_5Fe_9S_{18}$ (Ref. 23), plagioclase (Ref. 24), $K_5\{H[ON(SO_3)_2]_2\}\cdot 1.5H_2O$ (Ref. 25)
Conducting crystals with displacive modulation (and CDW?)	
One dimensional:	$K_2Pt(CN)_4Br_{0.3}\cdot xH_2O$ (Refs. 26, 27), PTZ – TCNQ (Ref. 28), $(TTF)_7I_5$ (Ref. 29), $(TMTTF)_{1.3}(TCNQ)_2$, $(C_{10}H_{12}S_4)_{1.3}(C_{12}H_4N_4)_2$ (Ref. 30),
Two and three dimensional:	TaS_2 (Refs. 31–33), $TaSe_2$ (Refs. 34, 35), $TaTe_2$ (Ref. 36), $NbTe_2$ (Ref. 32), $NbSe_2$ (Ref. 35), In_2Se_3 (Ref. 36).
Occupation waves and concentration waves	
	TaS_2 (Ref. 37), CuAu II (Ref. 38), $La_2O_3-CeO_2$ (Ref. 39), $Fe_{1-x}S$ (Ref. 40), $Fe_{1-x}O$ (Ref. 41), Plagioclase (Refs. 24, 42), Labradorite (Ref. 43)
Spin-density waves	
	Cr (Ref. 44, 45) (and others)
Helical magnetic structures	
	$MnAu_2$ (Ref. 46), Er (Ref. 47), Tm (Refs. 48, 49) (and others)

APPENDIX B: SPACE-TIME SYMMETRY THAT CAN OCCUR IN A VIBRATING CRYSTAL OF THE Na_2CO_3 TYPE ($G_0=C2/m$) IN THE SINGLE-MODE APPROXIMATION

In Table II, four-dimensional space groups are indicated compatible with normal-mode vibrational modes $\vec{q}$ occuring in the Na_2CO_3 structure. The basis vectors generating the lattice Λ_4 are according to Eq. (2.28) given by

$$a_i=(\vec{a}_i,\vec{q}\cdot\vec{a}_i/\omega_{\vec{q}\lambda}),\quad i=1,2,3,$$

and

$$a_4=(0,-2\pi/\omega_{\vec{q}\lambda}),$$

TABLE II. Four-dimensional space groups compatible with $C2/m$.

Wave vector $\vec{q}$	Lattice Λ_4		Occurring four-dimensional space group (Ref. 14)		
of the mode	Generators	Bravais class	Centering	Point group	Extensions
$O=(0,0,0)$	a_1-a_2,a_4,a_1+a_2,a_3	IV D	D	$2/m\,1'$	$0,e_1,e_5,e_1+e_5$
$A=(0,0,\frac{1}{2})$	$a_4,a_1-a_2,2a_3-a_4,$ a_1+a_2	IV G	G	$2/m\,1'$	$0,e_1$
$R=(\frac{1}{2},\frac{1}{2},0)$	$a_4,a_1-a_2,a_1+a_2-a_4,$ a_3	IV V	V	$2/m\,1'$	$0,e_4,e_5,e_4+e_5$
$S=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$a_4,a_1-a_2,a_1+a_2-2a_3,$ $2a_3-a_4$	IV G	G	$2/m\,1'$	$0,e_1$
$BR=(1-\alpha,\alpha,0)$	a_3,a_1+a_2,a_1-a_2,a_4	III M	M	$2/m'$	$0,e_1$
$CS=(1-\alpha,\alpha,\frac{1}{2})$	$a_1+a_2,2a_3-a_4,$ a_1-a_2,a_4	III G	G	$2/m'$	0
$M=(\alpha,\alpha,\beta)$	a_1-a_2,a_1+a_2,a_4,a_3	II C	C	$\bar{1}1'$	$0,e_1$
$T=(\frac{1}{2},0,0)$	$a_4,2a_1-a_4,a_2,a_3$	II C	C	$\bar{1}1'$	$0,e_1$
$D=(\frac{1}{2},0,\frac{1}{2})$	$a_4,2a_1-a_4,a_2,$ a_1-a_3	II C	C	$\bar{1}1'$	$0,e_1$

where the $\vec{a}_i$ span the basis of Λ_3 indicated in Fig. 2. There the fundamental cell of Λ_3^* spanned by the reciprocal basis $\{\vec{a}_i^*\}$ is also indicated. The fundamental region of the BZ is: *OBPACQ*. The Bravais classes and the space group in four-dimensions are noted following the conventions used in Ref. 14. In particular the centering looks as follows:

$$D=\tfrac{1}{2}0\tfrac{1}{2}0,\quad G=\tfrac{1}{2}0\tfrac{1}{2}0,\quad 0\tfrac{1}{2}0\tfrac{1}{2},\quad \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},$$

$$V=\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}0,\quad M=0\tfrac{1}{2}\tfrac{1}{2}0,\quad C=\tfrac{1}{2}\tfrac{1}{2}00.$$

APPENDIX C: FOUR-DIMENSIONAL SPACE GROUPS G COMPATIBLE WITH THE SPACE GROUP $G_m = C2/m$ OF THE AVERAGE STRUCTURE, AND WITH A BASIC SATELLITE VECTOR b_1^* LYING IN THE MIRROR PLANE

The basis $\{\vec{a}_i\}$ chosen for the lattice Λ_3 of the reference structure is indicated in Fig. 2 (see Appendix B). The group G_m is generated by

$$\{\vec{a}_1,\vec{a}_2,\vec{a}_3,m_y,2_y,\bar{1}\},\qquad\text{(C1)}$$

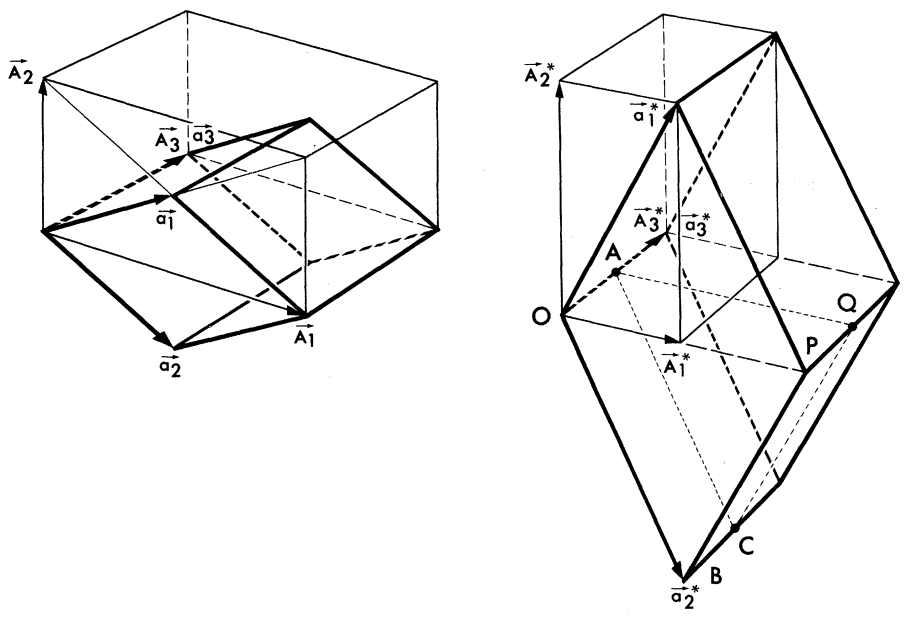

FIG. 2. Direct and reciprocal unit cell for $C2/m$ (unique axis y).

where $\vec{a}_2 - \vec{a}_1$ is oriented along the positive y axis (unique axis). Furthermore $\vec{a}_2 - \vec{a}_1 \perp \vec{a}_3$ and $\vec{a}_2 - \vec{a}_1 \perp \vec{a}_1 + \vec{a}_2$. The wave vector is $\vec{b}_1^* = \alpha\vec{a}_1^* + \alpha\vec{a}_2^* + \beta\vec{a}_3^*$ (see Appendix B). The little group $G_{\vec{q}}$ [defined in (2.22)] is generated by

$$\{\vec{a}_1, \vec{a}_2, \vec{a}_3, m_y\}, \tag{C2}$$

and $M_{\vec{q}}$ [see (2.35)] is given by

$$M_{\vec{q}} = \bar{1}G_{\vec{q}}.$$

The four-dimensional lattice translation group U is generated by

$$\begin{aligned} &a_1 = (\vec{a}_1, \alpha\vec{b}_1), \quad a_2 = (\vec{a}_2, \alpha\vec{b}_1), \\ &a_3 = (\vec{a}_3, \beta\vec{b}_1), \quad a_4 = (0, \vec{b}_1). \end{aligned} \tag{C3}$$

It depends on the properties of the Fourier components $\hat{\rho}(\vec{k})$, which elements of G_m admit a compensating internal transformation. We have in particular: writing $g = \{R\,|\,\vec{a}\}$ and using for R the magnetic notation $(R_E \oplus 1 \sim R_E, R_E \oplus \bar{1} \sim R_E')$

$$\begin{aligned} &\{m_y\,|\,(0, \vec{v})\} \in G \ \text{ if } \hat{\rho}(\vec{K} + z\vec{b}_1^*) = e^{-iz\vec{b}_1^* \cdot \vec{v}}\hat{\rho}(m_y\vec{K} + z\vec{b}_1^*), \\ &\{\bar{1}'\,|\,(0, \vec{v})\} \in G \ \text{ if } \hat{\rho}(\vec{K} + z\vec{b}_1^*) = e^{iz\vec{b}_1^* \cdot \vec{v}}\hat{\rho}(-\vec{K} - z\vec{b}_1^*), \\ &\{2_y'\,|\,(0, \vec{v})\} \in G \ \text{ if } \hat{\rho}(\vec{K} + z\vec{b}_1^*) = e^{iz\vec{b}_1^* \cdot \vec{v}}\hat{\rho}(2_y\vec{K} - z\vec{b}_1^*), \end{aligned} \tag{C4}$$

where $\vec{K} \in \Lambda_3^*$ and $z \in Z$. These relations are a consequence of (4.22), and can give rise to extinctions as indicated in Table III. As in Appendix B the notation used for the four-dimensional space group G is that adopted in Ref. 14.

APPENDIX D: THE STRUCTURE OF Na_2CO_3 (REF. 4)

The compound Na_2CO_3 is known to exist in three different solid phases, called the α, β, and γ phase: (i) α phase: above 489 °C; hexagonal structure; space group $G(\alpha) = P6_3/\text{mmc}$. (ii) β phase: between 360 and 489 °C; monoclinic structure; space group $G(\beta) = C2/\text{m}$. (iii) γ phase: below 360 °C; modulated structure; Euclidean space group $p1$ (one dimensional).

Basic structure: $G_0 = C2/m$;

Positions $\vec{r}_j$:		j
2Na(1):	(0 , 0 , 0)	1
2Na(2):	(0 , 0 , 0.5000)	2
4Na(3):	(0.1706, 0.5000, 0.7478)	3,
4C :	(0.1641, 0.5000, 0.2496)	5,
40(2) :	(0.2897, 0.5000, 0.1771)	7,
80(1) :	(0.1016, 0.2940, 0.2855)	8,

There are 24 atoms in the unit cell of the centered lattice (see Fig. 2). The six positions $\vec{r}_j$ indicated are given relative to the basis $\vec{A}_1, \vec{A}_2, \vec{A}_3$. The positions of the remaining 18 atoms can be obtained by applying appropriate space group elements to the indicated six positions. The primitive translations are generated by $\vec{a}_1 = \frac{1}{2}(\vec{A}_1 + \vec{A}_2)$, $\vec{a}_2 = \frac{1}{2}(\vec{A}_1 - \vec{A}_2)$, and $\vec{a}_3 = \vec{A}_3$.

Average structure: $G_m = C2/m$. Modulation: single-mode modulation: wave vector $\vec{q} = 0.182\vec{A}_1^* + 0.318\vec{A}_3^*$ (room temperature) going continuously to $0.154\vec{A}_1^* + 0.286\vec{A}_3^*$ (300 °C).

Polarization j	$\vec{f}_j(\vec{q})$ (relative to $\vec{A}_1, \vec{A}_2, \vec{A}_3$)
1	$(0, 0.0284e^{0.5\pi i}, 0)$
2	$(0, 0.0328e^{0.818\pi i}, 0)$
3	$(0, 0.0345e^{1.062\pi i}, 0)$
5	$(0, 0.0294e^{0.713\pi i}, 0)$
7	$(0, 0.0128e^{0.816\pi i}, 0)$
8	$(0.0166e^{1.53\pi i}, 0.0387e^{0.689\pi i}, 0.0215e^{1.385\pi i})$

Four-dimensional space group: $G = C2'/m, e_1$, generated by

TABLE III. Four-dimensional space groups for modulated crystals with average structure $C2/m$ and basic satellite reflection in the mirror plane.

Space group G	Point group K	Nonprimitive translations	Space group extinctions
$C\bar{1}1', 0$	$2'/m$	⋯	⋯
$C\bar{1}1', e_1$	$2'/m$	$p(m_y) = \frac{1}{2}a_4$	$\rho(K + z\vec{b}_1^*)$ for $m_y\vec{K} = \vec{K}$ and z odd
$C1', 0$	m	⋯	⋯
$C1', e_1$	m	$p(m_y) = \frac{1}{2}a_4$	$\rho(\vec{K} + z\vec{b}_1^*)$ for $m_y\vec{K} = \vec{K}$ and z odd
$P\bar{1}'$	$\bar{1}'$	⋯	⋯
$P\bar{1}$	$2'$	⋯	⋯
$P1$	1	⋯	⋯

$$(\{1|\vec{a}_i\},\{1|(\vec{q}\cdot\vec{a}_i/|\vec{q}|^2)\vec{q}\}),\quad i=1,2,3$$

$$(\{1|0\},\{1|\vec{b}\}),\quad \text{with } \vec{b}=(2\pi/|\vec{q}|^2)\vec{q}$$

generating U,

$$(\{m_y|0\},\{1|\tfrac{1}{2}\vec{b}\}),$$

$$(\{2_y|0\},\{-1|\tfrac{1}{2}\vec{b}\}).$$

The group G is equivalent to $C\bar{1}1'$, e_1 occurring in Table II for the $\vec{q}$ vector M.

Fourier components $\vec{f}_j(\vec{q})$ transform according to Eq. (3.16): for $(\{R_E|0\},\{R_I|\vec{a}_I\})\in G$ one has the following: If

$$R_E=\bar{1},\quad R_I=-1,\quad \vec{a}_I=0,$$

then

$$\vec{f}_{j'}(\vec{q})=-\vec{f}_j^{\,*}(q)e^{-i\vec{q}\cdot\vec{u}(R_E,j)};$$

if

$$R_E=m_y,\quad R_I=+1,\quad \vec{a}_I=\tfrac{1}{2}\vec{b},$$

then

$$\vec{f}_{j'}(\vec{q})=2_y\vec{f}_j(\vec{q});$$

if

$$R_E=2_y,\quad R_I=-1,\quad \vec{a}_I=\tfrac{1}{2}\vec{b},$$

then

$$\vec{f}_{j'}(\vec{q})=m_y\vec{f}_j^{\,*}(\vec{q})e^{-i\vec{q}\cdot\vec{u}(R_E,j)}.$$

APPENDIX E: AVERAGE STRUCTURE AND BASIC STRUCTURE FOR A CRYSTAL WITH A SINGLE-$\vec{q}$ PERIODIC DISTORTION (IN THE POINT-PARTICLE APPROXIMATION)

Consider the periodically distorted crystal described by the following density function:

$$\rho(\vec{r})=\sum_{\vec{n}\in\Lambda_3}\sum_{j=1}^{s}m_j\times\delta(\vec{r}-\vec{r}_0(\vec{n},j)-\vec{f}_j\sin(\vec{q}\cdot\vec{n}+\phi_j)),\tag{E1}$$

where use has been made of the notation adopted in Sec. III, and $\vec{q}\in\text{BZ}$.

Using the Jacobi-Anger generating function for Bessel functions

$$J_l(z)=\frac{1}{2\pi}\int_0^{2\pi}d\phi\, e^{i(-l\phi+z\sin\phi)},\quad z\in C,\ \phi\in R,\ l\in Z\tag{E2}$$

and inversely,

$$e^{iz\sin\phi}=\sum_{l=-\infty}^{\infty}e^{il\phi}J_l(z),\tag{E3}$$

one gets for the Fourier components

$$\hat{\rho}(\vec{k})=\sum_{j=1}^{s}\sum_{l=-\infty}^{\infty}m_je^{-\vec{k}\,\vec{r}_j+il\phi_j}J_l(-\vec{k}\cdot\vec{f}_j)\times\sum_{\vec{K}\in\Lambda_3^*}\delta(\vec{k}-\vec{K}-l\vec{q}).\tag{E4}$$

We associate the reflections $\vec{k}\equiv l\vec{q}\,(\text{mod}\,\Lambda_3^*)$, $l\neq 0$, with the satellites. Thus D_1^* is generated by $\vec{b}_1^{\,*}=\vec{q}$. Then condition (4.5) of Sec. IV implies

$$l\vec{q}\in\Lambda^*\ \text{ only for } l=0,$$

i.e., $\rho(\vec{r})$ describes a modulated structure. Note that even if one has a single-$\vec{q}$ distortion all multiples of $\vec{q}$ occur, in principle, in S_s. The reference structure is then given by

$$\rho_0(\vec{r})=\sum_{\vec{n}\in\Lambda_3}\sum_{j=1}^{s}m_j\delta(\vec{r}-\vec{r}_0(\vec{n},j))\tag{E5}$$

and the average structure by

$$\rho_m(\vec{r})=\frac{1}{2\pi}\int_0^{2\pi}d\phi\sum_{\vec{n}\in\Lambda_3}\sum_{j=1}^{s}m_j\times\delta(\vec{r}-\vec{r}_0(\vec{n},j)-\vec{f}_j\sin\phi).\tag{E6}$$

Introducing a function $\Delta(\vec{r})$ as

$$\Delta_j(\vec{r})=\begin{cases}(1/\pi)(1-\lambda^2)^{-1/2}\\ 0\ \text{otherwise,}\end{cases}$$

one can write

$$\rho_m(\vec{r})=\sum_{\vec{n}j}m_j\Delta_j(\vec{r}-\vec{r}_0(\vec{n},j)).\tag{E7}$$

Notice that Eq. (E6) is a special case of

$$f_m(\vec{r})\equiv\sum_{\vec{k}\in\Lambda_3^*}\hat{f}(\vec{k})e^{i\vec{k}\cdot\vec{r}}=\lim_{N\to\infty}\frac{1}{N}\sum_{\vec{n}\in\Lambda_3}f(\vec{r}-\vec{n}),$$

which expresses the average distribution of the function $f(\vec{r})$ over a unit cell of Λ_3.

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