PHYSICAL REVIEW B VOLUME 21, NUMBER 8 15 APRIL 1980

Wreath groups—symmetry of crystals with structural distortions

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(Received 4 December 1979)

A new class of groups is defined for describing the symmetry of atom arrangements in crystals with structural distortions. The general structure of these new groups, which we name wreath groups, is determined in a mathematically rigorous manner. Wreath groups are particularly suitable for describing atom arrangements in crystals with periodic structural distortions. The effect of such wreath-group symmetry on x-ray-diffraction patterns is briefly discussed. A new Bloch theorem, based on wreath-group symmetry, is formulated for crystals with structural distortions. This new Bloch theorem is applied to determine the form and corresponding charge density of one-electron eigenfunctions in the nearly-free-electron approximation for crystals with periodic structural distortions.

I. INTRODUCTION

Three-dimensional crystallographic space-group symmetry has for a long time been considered the main or fundamental characteristic of solid-state systems.[1-3] From the theory of the three-dimensional space groups follow important consequences concerning the physical properties of crystals, such as the Bloch theorem,[4] and one is able to predict such physical properties as energy degeneracies,[5] selection rules,[6] and characteristic x-ray-diffraction patterns.[7] In recent years one has become increasingly aware of the existence of solid-state systems with long-range order whose symmetry is not a three-dimensional crystallographic space group. Examples of such solid-state systems are γ-Na_2CO_3,[8] $NaNO_2$,[9] and K_2MoO_4,[10] ionic crystals with incommensurate periodic structural distortions, $(TTF)_7I_5$,[11] and TaS_2,[12] $TaSe_2$,[13] and $TaTe_2$,[14] layered transition-metal dichalcogenides with periodic structural distortions. Physical properties of such systems, as the characteristic three-dimensional x-ray-diffraction pattern, cannot be predicted nor understood using the theory of the three-dimensional crystallographic space groups.

One method of describing the symmetry of crystals with structural distortions has been introduced by de Wolff,[15] de Wolff,[15,16] and Janner and Janssen[17] describe a crystal with structural distortions in a suitably defined higher than three-dimensional space, the crystal with structural distortions being a three-dimensional section of this higher than three-dimensional space. The mathematical theory of the symmetry groups of this higher than three-dimensional space used to characterize crystals with structural distortions, called superspace groups, has been determined by Janner[18] and Janssen.[19]

The description of the symmetry of crystals with structural distortions to be developed in this paper is based on the use of a new class of symmetry groups. The method of defining such new groups is in turn based on the introduction of new types of operators by coupling additional suitably defined operators to the elements of three-dimensional crystallographic space groups. Such an approach to defining new groups has been used by Litvin[20,21] and Litvin and Opechowski[22] in defining spin groups. The additional operators coupled to elements of three-dimensional space groups introduced in this paper give rise to new symmetry groups whose mathematical structure is related to the mathematical concept of wreath products.[23,24] Consequently, these new groups have been named wreath groups.

A similar approach to the introduction of new groups of similiar mathematical structure, called generalized color groups, has been used by Koptsik and Kotzev,[25] and Koptsik.[26] The generalized color groups used to describe crystals with structural distortions[26,27] differ from the groups to be defined in this paper in details of their mathematical structure and in the type of additonal operators coupled to elements of the three-dimensional crystallographic space groups.

In Sec. II, after a brief review of terminology, we introduce new types of operators by coupling additional operators to elements of the three-dimensional crystallographic space groups to describe the symmetry of crystals with structural distortions. New symmetry groups of crystals with structural distortions, named wreath groups, are then defined. The mathematical structure of wreath groups is determined in Sec. III and the effect of such wreath-group symmetry on x-ray-diffraction patterns is briefly discussed in Sec. IV. In Sec. V, a new Bloch theorem based on wreath-group symmetry and applicable to crystals with structural distortions is formulated. This Bloch theorem is then applied to determine the form of the one-electron eigenfunctions and corresponding charge density in the nearly-free-electron approximation for crystals with periodic structural distortions.

II. WREATH GROUPS OF CRYSTALS WITH STRUCTURAL DISTORTIONS

We use the following notation and terminology[22]: $E_s(3)\times E_t(1)$ is "space-time," the product space of a three-dimensional Euclidean point space called "space" and a one-dimensional Euclidean point space called "time." $(\vec{r}, t)$ is a point in space-time in some coordinate system. $\mathcal{E}_s(3)\times\mathcal{E}_t(1)$ is the Newton group, the direct product of the Euclidean group $\mathcal{E}_s(3)$ consisting of all proper and improper rotations and all translations of $E_s(3)$, and the Euclidean group $\mathcal{E}_t(1)$ consisting of time inversion and all time translations of $E_t(1)$. An element of $\mathcal{E}_s(3)$ will be denoted by $F=(R\,|\,\vec{v})$ where R is a three by three proper or improper rotation matrix and $\vec{v}$ is a three by one column translation matrix. An element of $\mathcal{E}_t(1)$ is denoted by $(A\,|\,\tau)$ where A is an element of the time-inversion group $\underline{A}$ consisting of the unit element $E=1$ and time-inversion $E'=-1$, and τ is any real number representing a time translation.

A crystal is a subset $C_s(3)$ of points in $E_s(3)$, the points being the positions at which atoms are located. A crystal $C_s(3)$ is invariant under an element F of $\mathcal{E}_s(3)$, and F is said to be a symmetry element of the crystal if, for each $\vec{r}$ of $C_s(3)$

$$F\vec{r}=(R\,|\,\vec{v})\vec{r}=R\vec{r}+\vec{v},$$

is also a point of $C_s(3)$. The set of all such symmetry elements F constitutes a group $\underline{F}$ called the symmetry group of the crystal. We shall restrict the meaning of a "crystal $C_s(3)$" in this paper to that of a subset of points in $E_s(3)$ whose symmetry group is one of the 230 three-dimensional crystallographic space groups.

Consider a subset $C_s(3)\times E_t(1)$ of space-time. A crystal with structural distortions shall be defined here by a function $\vec{D}(\vec{r}, t)$ which maps points $(\vec{r}, t)$ of $C_s(3)\times E_t(1)$ to vectors $\vec{D}$ of a vector space V^-. V^- is a three-dimensional carrier space of the irreducible representation

$$((R\,|\,\vec{v}),(A\,|\,\tau))\to D_1^-(R\,|\,\vec{v})\times\Gamma^+(A\,|\,\tau)$$

of the Newton group, where $D_1^-(R\,|\,\vec{v})=R$ and $\Gamma^+(A\,|\,\tau)=+1$. The vector space V^- will be called the "distortion space" and vectors $\vec{D}$ "distortions." $\vec{D}(\vec{r}, t)$, for a specific $\vec{r}$ of $C_s(3)$ and specific t, is a vector which represents the structural distortion at time t of the atom of the crystal $C_s(3)$ at $\vec{r}$.

We shall restrict ourselves to the case of static structural distortions, the invariance of the structural distortions $\vec{D}(\vec{r}, t)$ under the time inversion group $\underline{A}$ and all translations τ being understood without being explicitly stated. Consequently, we shall write $\vec{D}(\vec{r})$ instead of $\vec{D}(\vec{r}, t)$. Because we consider only static structural distortions and because $C_s(3)$ is a crystal, we shall consider only the subgroup $\underline{F}$ of the Newton group, where $\underline{F}$ is the three-dimensional crystallographic space group of $C_s(3)$.

Because the distortion space V^- is a carrier space of the irreducible representation given above, a transformation F of the crystal $C_s(3)$ implies a transformation R of distortion space. Consequently, a crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ is transformed by an element F of $\underline{F}$ into the crystal $C_s(3)$ with structural distortions denoted by $[R\,\|\,F]\vec{D}(\vec{r})$ and defined by

$$[R\,\|\,F]D^i(\vec{r})=\sum_{j=1}^{3}R_{ij}D^j(F^{-1}\vec{r}). \tag{1}$$

We interpret the symbol $[R\,\|\,F]$ as an operator on the space of all structural distortions of a given crystal $C_s(3)$. The action of the operator $[R\,\|\,F]$ is twofold: The transformation F on the right-hand side of the double vertical bars acts only on the space $E_s(3)$ in which the crystal $C_s(3)$ is defined. The transformation R on the left-hand side acts only in the distortion space V^-.

A crystal with structural distortions $\vec{D}(\vec{r})$ is invariant under an element F of $\underline{F}$ if

$$[R\,\|\,F]\vec{D}(\vec{r})=\vec{D}(\vec{r}), \tag{2}$$

and F is said to be a symmetry element of the crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$. The set of all such symmetry elements constitutes a group $\underline{G}$ identical with or a subgroup of $\underline{F}$, the crystallographic symmetry group of the crystal $C_s(3)$.

Such a definition of the symmetry group of a crystal with structural distortions is in agreement with the usual definition of the symmetry group of a set of points in space: If the atomic positions of the crystal with structural distortions are written as $\vec{r}+\vec{D}(\vec{r})$, where $\vec{r}$ is a position of the undistorted crystal $C_s(3)$ and $\vec{D}(\vec{r})$ the structural distortion of the atom at the position $\vec{r}$, then $\underline{F}$ is a symmetry element if for each position $\vec{r}+\vec{D}(\vec{r})$

$$\begin{aligned}F\{\vec{r}+\vec{D}(\vec{r})\}&=(R\,|\,\vec{v})\{\vec{r}+\vec{D}(\vec{r})\}\\&=R\vec{r}+\vec{v}+R\vec{D}(\vec{r})\\&=F\vec{r}+R\vec{D}(\vec{r})\end{aligned}$$

is also an atomic position of the crystal with structural distortions. Since $\vec{r}$ is an atomic position of the crystal $C_s(3)$ and F is an element of the crystallographic symmetry group of $C_s(3)$, $F\vec{r}$ is also an atomic position of the crystal $C_s(3)$. Consequently for $F\{\vec{r}+\vec{D}(\vec{r})\}$ to be an atomic position of the crystal with structural distortions, one must have $R\vec{D}(\vec{r})=\vec{D}(F\vec{r})$, or rewritten in a modified form, $R\vec{D}(F^{-1}\vec{r})=\vec{D}(\vec{r})$. This last relationship follows immediately from Eqs. (1) and (2).

The usefulness of mathematically representing a crystal with structural distortions by a function $\vec{D}(\vec{r})$ defined on the undistorted crystal $C_s(3)$ and its symmetry in terms of operators $[R\|F]$ acting on the space of all structural distortions of the crystal $C_s(3)$, is that a generalization of the concept of the symmetry of crystals with structural distortions can be formulated in analogy with generalizations of the concept of the symmetry of spin arrangements.[20-22,28] Such a generalization is based on the introduction of new operators acting on the space of all structural distortions on a given crystal $C_s(3)$.

We introduce two new types of operators on the space of all structural distortions on a given crystal $C_s(3)$. The first type of operator is denoted by $[E\|F]$ where F is an element of the crystallographic symmetry group $\underline{F}$ of the crystal $C_s(3)$. The action of an operator $[E\|F]$ is defined as follows: A crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ is transformed by an operator $[E\|F]$ into a crystal $C_s(3)$ with structural distortions denoted by $[E\|F]\vec{D}(\vec{r})$ and defined by

$$[E\|F]\vec{D}(\vec{r})=\vec{D}(F^{-1}\vec{r}). \tag{3}$$

The action of an operator $[E\|F]$ is only on the space $E_s(3)$ in which the crystal $C_s(3)$ is defined. The transformation E on the left-hand side of the double vertical bars is the identity rotation of the distortion space V^{-}. The set of all operators $[E\|F]$, one for each element F of the symmetry group $\underline{F}$ of the crystal $C_s(3)$, and with the product of two such operators defined by

$$[E\|F_1][E\|F_2]=[E\|F_1F_2],$$

constitutes a group isomorphic to $\underline{F}$ which we shall denote by Ω_F.

The second type of new operator on the space of all structural distortions on a given crystal $C_s(3)$ is denoted by $[\vec{V}(\vec{r})\|E]$ where $\vec{V}(\vec{r})$ is a function which maps points $\vec{r}$ of the crystal $C_s(3)$ to distortions of the distortion space V^{-}. The action of this second type of operator is defined as follows: A crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ is transformed by an operator $[\vec{V}(\vec{r})\|E]$ into a crystal $C_s(3)$ with structural distortions denoted by $[\vec{V}(\vec{r}')\|E]\mathrm{D}(\vec{r})$ (the argument $\vec{r}$ of the function $\vec{V}(\vec{r})$ has been replaced by the symbol r' to distinguish it from the argument of $\vec{D}(\vec{r})$) and defined by

$$[\vec{V}(\vec{r}')\|E]\vec{D}(\vec{r})=\vec{D}(\vec{r})+\vec{V}(\vec{r}). \tag{4}$$

Since both $\vec{D}(\vec{r})$ and $\vec{V}(\vec{r})$, for a specific $\vec{r}$, are distortions, vectors of the same vector space V^{-}, the vector sum on the right-hand side of Eq. (4) is well defined. The action of an operator $[\vec{V}(\vec{r}')\|E]$ is only on the displacement space V^{-}, the symbol E on the right-hand side of the double vertical bars being the identity rotation of the space $E_s(3)$ in which the crystal $C_s(3)$ is defined. The action of an operator $[\vec{V}(\vec{r}')\|E]$ is position dependent. That is, the value of the function $\vec{V}(\vec{r}')$ added to the right-hand side of Eq. (4) is dependent on the value of the argument $\vec{r}$ of the structural distortion function $\vec{D}(\vec{r})$ on the left-hand side of Eq. (4).

The set of all operators $[\vec{V}(\vec{r})\|E]$, for all functions $\vec{V}(\vec{r})$ which map points $\vec{r}$ of the crystal $C_s(3)$ to vectors of the distortion space V^{-}, can be promoted to a group, which we denote by Ω_V by defining the product of two operators $[\vec{V}_1(\vec{r})\|E]$ and $[\vec{V}_2(\vec{r})\|E]$ as

$$[\vec{V}_1(\vec{r})\|E][\vec{V}_2(\vec{r})\|E]=[\vec{V}_1(\vec{r})+\vec{V}_2(\vec{r})\|E].$$

An operator $[\vec{V}(\vec{r})\|E]$ is a symmetry element of a crystal with structural distortions only if $\vec{V}(\vec{r})$ is the identity function $\vec{V}_E(\vec{r})$, the function which maps all points $\vec{r}$ of the crystal $C_s(3)$ to the null vector of the distortion space V^{-}. This follows from Eq. (4) which implies that $[\vec{V}(\vec{r})\|E]$ is a symmetry operator only if $\vec{D}(\vec{r})+\vec{V}(\vec{r})=\vec{D}(\vec{r})$. This relationship is satisfied by a function $\vec{V}(\vec{r})=0$ for all $\vec{r}$, i.e., if $\vec{V}(\vec{r})$ is the identity function $\vec{V}_E(\vec{r})$.

Although an operator $[\vec{V}(\vec{r})\|E]$ with $\vec{V}(\vec{r})\neq\vec{V}_E(\vec{r})$ is never a symmetry of a crystal with structural distortions, as we shall show below, a combination of the two new types of operators, $[\vec{V}(\vec{r})\|E]$ with $\vec{V}(\vec{r})\neq\vec{V}_E(\vec{r})$ defined in Eq. (4), and $[E\|F]$ defined in Eq. (3) can be a symmetry element.

We consider the set of all pairs $[\vec{V}(\vec{r})\|F]$ of operators $[\vec{V}(\vec{r})\|E]$ of the group Ω_V and operators $[E\|F]$ of the group Ω_F, where $\underline{F}$ is the crystallographic symmetry group of the crystal $C_s(3)$. The action of an operator pair $[\vec{V}(\vec{r})\|F]$ on a crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ transforms the crystal into the crystal $C_s(3)$ with structural distortions denoted by $[\vec{V}(\vec{r}')\|F]\vec{D}(\vec{r})$ and defined by

$$[\vec{V}(\vec{r}')\|F]\vec{D}(\vec{r})=\vec{D}(F^{-1}\vec{r})+\vec{V}(\vec{r}). \tag{5}$$

As in Eq. (4), the action of the operator pair defined here is position dependent. It follows from the definition of action, Eq. (5), that the product of two operator pairs $[\vec{V}_1(\vec{r})\|F_1]$ and $[\vec{V}_2(\vec{r})\|F_2]$ is given by

$$[\vec{V}_1(\vec{r})\|F_1][\vec{V}_2(\vec{r})\|F_2]$$
$$=[\vec{V}_1(\vec{r})+\vec{V}_2(F_1^{-1}\vec{r})\|F_1F_2]. \tag{6}$$

The set of all pairs $[\vec{V}(\vec{r})\|F]$ of operators $[\vec{V}(\vec{r})\|E]$ of Ω_V and operators $[E\|F]$ of Ω_F together with the product defined in Eq. (6) constitutes a group, the semidirect product $\Omega_V \times_s \Omega_F$ of the group Ω_V by the group Ω_F. The identity element is $[\vec{V}_E(\vec{r})\|E]$ where $\vec{V}_E(\vec{r})$ is the identity function and E is the identity element of $\underline{F}$. The inverse of an element $[\vec{V}(\vec{r})\|F]$ is given by

$$[\vec{V}(\vec{r})\|F]^{-1} = [-\vec{V}(F\vec{r})\|F^{-1}]\,.$$

This semidirect product $\Omega_V \times_s \Omega_F$ is called the "wreath product" $\underline{V}^{-}\times_w\Omega_F$ of the distortion space V^{-} considered as an Abelian group $\underline{V}^{-}$ under vector addition, and the group Ω_F.[24,28]

A crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ is said to be invariant under an operator $[\vec{V}(\vec{r})\|F]$ of the wreath product $\underline{V}^{-}\times_w\Omega_F$ if

$$[\vec{V}(\vec{r}\,')\|F]\vec{D}(\vec{r}) = \vec{D}(\vec{r})\,, \tag{7}$$

for all $\vec{r}$ of the crystal $C_s(3)$. We shall say in such a case that $[\vec{V}(\vec{r})\|F]$ is a symmetry element of the crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$.

It follows from Eqs. (1) and (2) that F is a crystallographic symmetry element of a crystal with structural distortions $\vec{D}(\vec{r})$ if and only if $R\vec{D}(F^{-1}\vec{r}) = \vec{D}(\vec{r})$. This implies that F is a crystallographic symmetry element only if the magnitude of the distortions $\vec{D}(F^{-1}\vec{r})$ and $\vec{D}(\vec{r})$ for all $\vec{r}$ are the same. From Eqs. (5) and (7) it follows that $[\vec{V}(\vec{r})\|F]$ is a symmetry element if

$$\vec{D}(F^{-1}\vec{r}) + \vec{V}(\vec{r}) = \vec{D}(\vec{r})\,. \tag{8}$$

Consequently, unlike crystallographic symmetry elements, for an operator $[\vec{V}(\vec{r})\|F]$ to be a symmetry element, it is not necessary for the distortions $\vec{D}(\vec{r})$ and $\vec{D}(F^{-1}\vec{r})$ to be of the same magnitude.

The set of all symmetry elements $[\vec{V}(\vec{r})\|F]$ of a crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ constitutes a group, the symmetry group of the crystal with structural distortions. We now define a wreath group: A subgroup of the wreath product $\underline{V}^{-}\times_w\Omega_F$ will be called a "wreath group" if it is the symmetry group of some crystal $C_s(3)$ with some structural distortions $\vec{D}(\vec{r})$.

III. STRUCTURE OF WREATH GROUPS

In this section we discuss the structure of wreath groups, subgroups of wreath products $\underline{V}^{-}\times_w\Omega_F$ which are symmetry groups of crystals with structural distortions. Wreath groups are those subgroups of wreath products $\underline{V}^{-}\times_w\Omega_F$ consisting of a set of pairs of operators $[\vec{V}(\vec{r})\|F]$, one such pair for each element F of the crystallographic symmetry group $\underline{F}$ of the crystal $C_s(3)$. Wreath groups are isomorphic to $\underline{F}$. One can first show that the symmetry group of all crystals with structural distortions are such subgroups, and then show that every such subgroup is the symmetry group of a crystal with some structural distortion. The proof of these statements has been given in detail elsewhere.[28]

For each element F of the crystallographic symmetry group $\underline{F}$ of the crystal $C_s(3)$ there is a single function $\underline{\vec{V}(\vec{r})}$, which we shall denote as $\vec{V}_F(\vec{r})$, such that the operator pair $[\vec{V}_F(\vec{r})\|F]$ is a symmetry element of the crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$. For each F, the function $\vec{V}_F(\vec{r})$ is determined from Eq. (8), the condition that $[\vec{V}_F(\vec{r})\|F]$ is a symmetry element of the crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$. This condition, rewritten in a form to determine the function $\vec{V}_F(\vec{r})$ is

$$\vec{V}_F(\vec{r}) = \vec{D}(\vec{r}) - \vec{D}(F^{-1}\vec{r})\,. \tag{9}$$

Given a crystal $C_s(3)$ with structural distortions and knowing only the distorted positions of the atoms, there is a nonuniqueness in the choice of the positions of the atoms in the undistorted crystal $C_s(3)$. That is, a crystal $C_s(3)$ whose atom positions are at $\vec{r}$ and whose structural distortions are given by $\vec{D}(\vec{r})$ can equally be considered as the crystal $C_s'(3)$ whose atom positions are at $\vec{r}\,' = \vec{r} + \vec{a}$, where $\vec{a}$ is a constant vector, and whose structural distortions are given by $\vec{D}'(\vec{r}\,') = \vec{D}(\vec{r}) - \vec{a}$. However, the symmetry group of the crystal with structural distortions is not dependent on such a nonuniqueness in the choice of the atom positions of the crystal $C_s(3)$. The symmetry group of the crystal $C_s(3)$ with structural distortions $\vec{D}(\vec{r})$ is the set of all operator pairs $[\vec{V}_F(\vec{r})\|F]$ where $\vec{V}_F(\vec{r})$ is defined in Eq. (9). The symmetry group of this same crystal with structural distortions considered as the crystal $C_s'(3)$ with structural distortions $\vec{D}'(\vec{r}\,')$ is the set of all operator pairs $[\vec{V}_F'(\vec{r}\,')\|F]$ where $\vec{V}_F'(\vec{r}\,')$ is defined, again using Eq. (9), by

$$\begin{aligned}\vec{V}_F'(\vec{r}\,') &= \vec{D}'(\vec{r}\,') - \vec{D}'(F^{-1}\vec{r}\,')\\ &= \vec{D}(\vec{r}) - \vec{a} - [\vec{D}(F^{-1}\vec{r}) - \vec{a}]\\ &= \vec{D}(\vec{r}) - \vec{D}(F^{-1}\vec{r})\\ &= \vec{V}_F(\vec{r})\,.\end{aligned}$$

Consequently $\vec{V}_F'(\vec{r}\,') = \vec{V}_F(\vec{r})$, the value of the function $\vec{V}_F'(\vec{r}\,')$ at $\vec{r}\,' = \vec{r} + \vec{a}$ is the same as the value of the function $\vec{V}_F(\vec{r})$ at $\vec{r}$. The symmetry group of a crystal with structural distortions is then not dependent on the choice of the atom positions of the crystal.

As an example of a crystal $C_s(3)$ with structural distortions, we consider the incommensurate periodic structural distortions in the $1T$ polymorph of the layered transition-metal dichalcogenide TaS_2. A single layer of the layered transition metal dichalcogenide consists of three sheets of atoms, a top and bottom sheet of hexagonally packed chalcogen atoms, and a middle sheet of metal atoms. The crystallographic symmetry group of a crystal of TaS_2 is the space group $\underline{F} = P\bar{3}m1(D_{3d}^3)$. A single layer of the $1T$ polymorph is shown in Fig. 1.

A model of the structure of $1T$-TaS_2 in its incommensurate periodic structural distortion phase has structural distortions given by[13]

$$\vec{D}(\vec{r}) = \vec{U}(\vec{r}) + [3_z]\vec{U}(\vec{r}) + [3_z^2]\vec{U}(\vec{r}), \tag{10}$$

where

$$\vec{U}(\vec{r}) = \vec{A}\sin(\vec{Q}\cdot\vec{r} + \alpha),$$

$\vec{Q}$ is a vector in the reciprocal x-axis direction, $\vec{A}$ is parallel to $\vec{Q}$, and α is a phase factor which changes by 120° from one layer to the next. The structural distortions of one layer, taking $\alpha = 0$, is shown in Fig. 2.

The symmetry group of this crystal with structural distortions given by Eq. (10) is the subgroup of the wreath product $\underline{V}^{-}\times_w\Omega_F$ with $\underline{F} = P3m1\,(D_{3d}^3)$, a wreath group consisting of all operator pairs $[\vec{V}_F(\vec{r})\|F]$ with $\vec{V}_F(\vec{r})$ defined by Eq. (9), one such pair for each element of the space group $\underline{F}$.

IV. X-RAY DIFFRACTION

In this section we shall briefly consider the characteristic x-ray-diffraction pattern of a crystal with structural distortions, and in particular the case of a crystal with periodic structural distortions.[29,30] The intensity of the x-ray reflection corresponding to a scattering vector $\vec{k}$ is proportional to the modulus of the structure factor $F(\vec{k})$, which in the case of a crystal with structural distortions can be written as

$$F(\vec{k}) = \sum_i f_i \exp\{i\vec{k}\cdot[\vec{r}_i + \vec{D}(\vec{r}_i)]\},$$

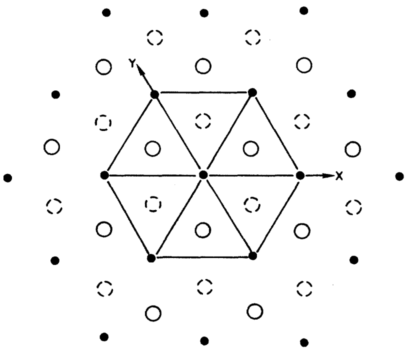

FIG. 1. Single layer of the $1T$ polymorph of the layered transition-metal dichalcogenides. The layer consists of three sheets of atoms, a top ○ sheet and bottom ◌ sheet of charcogen atoms, and a center sheet ● of metal atoms.

where $\vec{D}(\vec{r})$ is the structural distortion of the atom whose position in the crystal $C_s(3)$ is $\vec{r}$.

We shall consider a crystal $C_s(3)$ with structural distortions whose symmetry group is a wreath group, consisting of operator pairs $[\vec{V}_F(\vec{r})\|F]$ one such pair for each element F of the crystallographic symmetry group of the crystal $C_s(3)$. The wreath group contains a subgroup $\underline{T}_w$ consisting of operator pairs $[\vec{V}_t(\vec{r})\|\vec{t}]$ one such pair for each translation $\vec{t}$ of the translational subgroup $\underline{T}$ of $\underline{F}$. The structure factor can then be written as

$$F(\vec{k}) = \sum_j f_j \sum_t \exp\{i\vec{k}\cdot[\vec{r}_j - \vec{t} + \vec{D}(\vec{r}_j - \vec{t})]\},$$

where the summation is over all translations $\vec{t}$ of $\underline{T}$ and positions $\vec{r}_j$ of atoms in the primitive unit cell of the crystal $C_s(3)$. Since $[\vec{V}_t(\vec{r})\|\vec{t}]$ is a symmetry element of the crystal with structural distortions, using Eq. (8) for $F = \vec{t}$, we can rewrite the structure factor as

$$F(\vec{k}) = \sum_j f_j \exp\{i\vec{k}\cdot[\vec{r}_j + \vec{D}(\vec{r}_j)]\}$$
$$\times\sum_t \exp\{-i\vec{k}\cdot[\vec{t} + \vec{V}_t(\vec{r}_j)]\}. \tag{11}$$

We shall consider the case of a crystal with periodic structural distortions and assume that the structural distortions are of the form $\vec{D}(\vec{r}) = \vec{A}\sin\vec{Q}\cdot\vec{r}$. In this case, using Eq. (8), one has that the term containing the summation over $\vec{t}$ in Eq. (11) is proportional to

$$\sum_t e^{-i\vec{k}\cdot\vec{t}} \exp[-i\vec{k}\cdot\vec{A}\sin\vec{Q}\cdot(\vec{r}_j - \vec{t})].$$

Using the Jacobi-Auger expansion[31]

$$e^{ix\sin\theta} = \sum_{m=-\infty}^{+\infty} e^{im\theta} J_m(x), \tag{12}$$

where J_m are Bessel functions of the first kind,

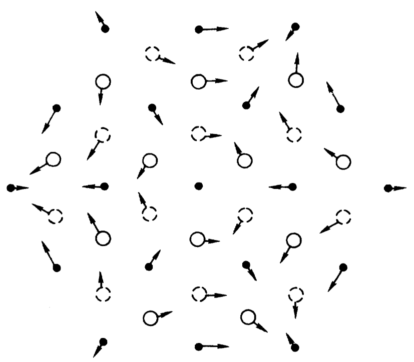

FIG. 2. Model of the incommensurate structural distortions of a single layer of $1T$-TaS_2 discussed in the text. The distortions are greatly exaggerated.

this term becomes

$$\exp(-i\vec{k}\cdot\vec{A}\vec{Q}\cdot\vec{r}_j)\sum_m J_m(-i\vec{k}\cdot\vec{A})$$
$$\times\sum_t \exp[-i(\vec{k}+m\vec{Q})\cdot\vec{t}]\,.$$

Finally, since the summation over $\vec{t}$ is proportional to $\delta(\vec{K}-\vec{k}-m\vec{Q})$, where $\vec{K}$ is a reciprocal-lattice vector of the crystal $C_s(3)$, one has that the structure factor and consequently the intensity, can be nonzero only for scattering vectors $\vec{k}$ which satisfy the relationship $\vec{k}=\vec{K}+m\vec{Q}$. We can write

$$F(\vec{k})=\sum_{\vec{K},m} F(\vec{k})\delta(\vec{k}-\vec{K}-m\vec{Q})\,.$$

Reflections corresponding to the case $\vec{k}=\vec{K}$, i.e., with $m=0$, are known as main reflections, and for $\vec{k}=\vec{K}+m\vec{Q}, m\neq 0$, as satellite reflections. For the model of the incommensurate periodic structural distortion phase of the layered transition-metal dichalcogenide $1T$–TaS_2 with structural distortions given by Eq. (10), the structure factor can be written as

$$F(\vec{k})=\sum_{\vec{K},m_1,m_2,m_3} F(\vec{k})\delta(\vec{k}-\vec{K}-m_1\vec{Q}-m_2[3_z]\vec{Q}$$
$$-m_3[3_z^2]\vec{Q})\,.$$

The main reflections for $\vec{k}=\vec{K}$ and satellite reflections for

$$\vec{k}=\vec{K}+m_1\vec{Q}+m_2[3_z]\vec{Q}+m_3[3_z^2]\vec{Q}\,,$$

where at least one of m_1, m_2, and m_3 is nonzero.

V. BLOCH THEOREM FOR CRYSTALS WITH STRUCTURAL DISTORTIONS

In this section we investigate the structure of the eigenfunctions of the electronic Schrödinger equation in the case of a crystal with structural distortions, and in particular in the case of a crystal with periodic structural distortions. We first briefly review the transformational properties of time-independent scalar functions under transformations of space-time and then define the transformational properties of such functions under new operators similiar to those introduced in Sec. II. We then derive a Bloch theorem applicable to the structure of electronic eigenfunctions of crystals with structural distortions. Consider a scalar function ω defined in space-time. That is, we consider a function ω which maps points $(\vec{r}, t)$ of $E_s(3)\times E_t(1)$ into the field of complex numbers. We consider only static scalar functions and consequently shall denote this function as $\omega(\vec{r})$ instead of $\omega(\vec{r}, t)$, the invariance of $\omega(\vec{r})$ under $\mathcal{E}_t(1)$ being understood without being explicitly stated. A function $\omega(\vec{r})$ transforms under an element F of $\mathcal{E}_s(3)$ as follows: An element F of $\mathcal{E}_s(3)$ transforms a function $\omega(\vec{r})$ into the function denoted by $[F]\omega(\vec{r})$ and defined by

$$[F]\omega(\vec{r})=\omega(F^{-1}\vec{r})\,. \tag{13}$$

We interpret the symbol $[F]$ in this equation as an operator on the space of all scalar functions defined on $E_s(3)$.

We introduce new more general operators on the space of all scalar functions defined on $E_s(3)$. These operators are of the form $[V(\vec{r})\|F]$, elements of the wreath product $\underline{V}^{-}\times_w\Omega_{E_s(3)}$, similar to the operators introduced in Sec. II. The difference is that here F is an element of the Euclidean group $\mathcal{E}_s(3)$ and $\vec{V}(\vec{r})$ is a function which maps all points $\vec{r}$ of $E_s(3)$ into the distortion space V^{-}.

A scalar function $\omega(\vec{r})$ can and shall be considered a function $\omega(\vec{r}+\vec{V}_E(\vec{r}))$, where $\vec{V}_E(\vec{r})$ is the identity function which maps all points $\vec{r}$ of the space $E_s(3)$ to the null vector of distortion space. We define the action of an operator pair $[\vec{V}(\vec{r})\|F]$ of the wreath product $\underline{V}^{-}\times_w\Omega_{E_s(3)}$ on a scalar function $\omega(\vec{r}+\vec{V}_E(\vec{r}))$ as follows: An operator $[\vec{V}(\vec{r})\|F]$ transforms a function $\omega(\vec{r}+\vec{V}_E(\vec{r}))$ into a function denoted by $[\vec{V}(\vec{r}\,')\|F]\omega(\vec{r}+\vec{V}_E(\vec{r}))$ [where the argument $\vec{r}$ of the function $\vec{V}(\vec{r})$ has been replaced by $\vec{r}\,'$ to distinguish it from the argument of the function ω] and defined by

$$[\vec{V}(\vec{r}\,')\|F]\omega(\vec{r}+\vec{V}_E(\vec{r}))$$
$$=\omega(F^{-1}\vec{r}+\vec{V}_E(\vec{r})-\vec{V}(\vec{r}))\,. \tag{14}$$

The action of the right-hand side component F of the operator pair $[\vec{V}(\vec{r}\,')\|F]$ is only on the space component $\vec{r}$ of the argument of the function $\omega(\vec{r}+\vec{V}_E(\vec{r}))$. The action of the left-hand side component $\vec{V}(\vec{r}\,')$ of the operator pair $[\vec{V}(\vec{r}\,')\|F]$ is only on the distortion space component $\vec{V}_E(\vec{r})$. The latter is position dependent, that is, the value of the function $\vec{V}(\vec{r}\,')$ which is added to the argument of the function ω on the right-hand side of Eq. (14) is dependent on the value of the space component $\vec{r}$ of the function ω on the left-hand side of Eq. (14).

It follows from the definition of action of operators $[F]$ given in Eq. (13) and of operators $[\vec{V}(\vec{r})\|F]$ in Eq. (14), that operators $[F]$ are a special case of operators $[\vec{V}(\vec{r})\|F]$. Operators $[F]$ are operators of the form $[\vec{V}_E(\vec{r})\|F]$. It also follows from Eq. (14) that the product of two operator pairs $[\vec{V}_1(\vec{r})\|F_1]$ and $[\vec{V}_2(\vec{r})\|F_2]$ is given by Eq. (6). That is, since

$$[\vec{V}_1(\vec{r}\,')\| F_1][\vec{V}_2(\vec{r}\,'')\| F_2]\,\omega(\vec{r}+\vec{V}_E(\vec{r})) = [\vec{V}_2(\vec{r}\,'')\| F_2]\,\omega(F_1^{-1}\vec{r}+\vec{V}_E(\vec{r})-\vec{V}_1(\vec{r}))$$
$$= \omega(F_2^{-1}F_1^{-1}\vec{r}+\vec{V}_E(\vec{r})-\vec{V}_1(\vec{r})-\vec{V}_2(F_1^{-1}\vec{r}))$$
$$= [\vec{V}_1(\vec{r}\,')+\vec{V}_2(F_1^{-1}\vec{r}\,')\| F_1F_2]\,\omega(\vec{r}+\vec{V}_E(\vec{r}))\,,$$

it follows that:

$$[\vec{V}_1(\vec{r})\| F_1][\vec{V}_2(\vec{r})\| F_2] = [\vec{V}_1(\vec{r})+\vec{V}_2(F_1^{-1}\vec{r})\| F_1F_2]\,.$$

The Bloch theorem[4] is a statement concerning the structure of the eigenfunctions $\psi(\vec{r})$ of the electronic Schrödinger equation of a crystal $C_s(3)$

$$H\psi(\vec{r})=E\psi(\vec{r})\,. \tag{15}$$

Its derivation is based on a relationship between the symmetry group of the crystal $C_s(3)$ and the symmetry group of the Hamiltonian H of the Schrödinger equation. In the case of crystals $C_s(3)$, the crystallographic space group $\underline{F}$ of the crystal $C_s(3)$ is an invariance group of the Hamiltonian H. This space group $\underline{F}$ contains an invariant subgroup T of translations whose elements are denoted by t. The irreducible representations of this Abelian subgroup of translations are one-dimensional irreducible representations $\Gamma^{\vec{k}}$, where $\Gamma^{\vec{k}}(\vec{t}) = e^{i\vec{k}\cdot\vec{t}}$, indexed by vectors $\vec{k}$ in the first Brillouin zone. The eigenfunctions $\psi(\vec{r})$ are then classified according to the irreducible representations $\Gamma^{\vec{k}}$ of $\underline{T}$, indexed by $\vec{k}$, and denoted by $\psi_{\vec{k}}(\vec{r})$. The Bloch theorem states that the structure of the eigenfunctions $\psi_{\vec{k}}(\vec{r})$ are such that

$$\psi_{\vec{k}}(\vec{r})=e^{-i\vec{k}\cdot\vec{r}}U_{\vec{k}}(\vec{r}),$$
$$[\vec{t}\,]\,U_{\vec{k}}(\vec{r})=U_{\vec{k}}(\vec{r})\,.$$

The function $U_{\vec{k}}(\vec{r})$ is invariant under translations $\vec{t}$ of $\underline{T}$, that is, using Eq. (13), $U_{\vec{k}}(\vec{r}-\vec{t})=U_{\vec{k}}(\vec{r})$.

In the case of a crystal $C_s(3)$ with structural distortions, the symmetry group of the crystal with structural distortions is not the space group $\underline{F}$ but a wreath group, a subgroup of the wreath product $\underline{V}^{-}\times_w\Omega_F$ defined in Sec. II. Such a group consists of operator pairs $[\vec{V}_F(\vec{r})\| F]$, one such pair for each element F of $\underline{F}$ and such that the functions $\vec{V}_F(\vec{r})$ map points corresponding to atom positions of the crystal $C_s(3)$ to vectors in distortion space V^{-}. We shall assume the following relationship between the wreath-group symmetry of the crystal with structural distortions and an invariance group of the Hamiltonian of the Schrödinger equation given in Eq. (15): There exists an invariance group of the Hamiltonian, a subgroup of the wreath product $\underline{V}^{-}\times_w\Omega_{E_s(3)}$ consisting of operator pairs $[\mathrm{V}_F(\mathrm{r})\| F]$, one such pair for each element F of $\underline{F}$, and functions $\vec{V}_F(\vec{r})$ which map all points $\vec{r}$ of $E_s(3)$ to vectors in distortion space, such that by restricting the functions $\vec{V}_F(\vec{r})$ to points $\vec{r}$ corresponding to atom positions, this subgroup becomes identical with the wreath-group symmetry of the crystal with structural distortions.

Since the crystal with structural distortions is invariant under a wreath group, it then follows that the Hamiltonian is invariant under a group of operator pairs $\underline{T}_w$ consisting of operator pairs $[\vec{V}_t(\vec{r})\| \vec{t}\,]$, one such pair for each translation $\vec{t}$ of the translational subgroup $\underline{T}$ of $\underline{F}$. This group $\underline{T}_w$ of operator pairs is isomorphic to the group $\underline{T}$ and the irreducible representations of $\underline{T}_w$ are then identical with those of $\underline{T}$; i.e., $\Gamma^{\vec{k}}(\vec{V}_t(\vec{r})\|\vec{t}\,)=e^{-i\vec{k}\cdot\vec{t}}$. The action of an operator pair $[\vec{V}_t(\vec{r})\|\vec{t}\,]$ on an eigenfunction $\psi_{\vec{k}}(\vec{r})$ follows from Eq. (14):

$$[\vec{V}_t(\vec{r}\,')\|\vec{t}\,]\,\psi_{\vec{k}}(\vec{r})=\psi_{\vec{k}}(\vec{r}-\vec{t}-\vec{V}_t(\vec{r}))\,. \tag{16}$$

Since the irreducible representations of $\underline{T}_w$ are $\Gamma^{\vec{k}}$

$$[\vec{V}_t(\vec{r}\,')\|\vec{t}\,]\,\psi_{\vec{k}}(\vec{r})=e^{-i\vec{k}\cdot\vec{t}}\psi_{\vec{k}}(\vec{r})\,. \tag{17}$$

Assuming that the eigenfunctions $\psi(\vec{r})$ are of the form $\psi_{\vec{k}}(\vec{r})=e^{-\vec{k}\cdot\vec{r}}U_{\vec{k}}(\vec{r})$, substituting into Eqs. (16) and (17), and comparing right-hand sides, one finds

$$U_{\vec{k}}(\vec{r}-\vec{t}-\vec{V}_t(\vec{r}))=e^{-\vec{k}\cdot\vec{V}_t(\vec{r})}U_{\vec{k}}(\vec{r})\,, \tag{18}$$

which can be rewritten as

$$[\vec{V}_t(\vec{r}\,')\,\|\,\vec{t}\,]\,U_{\vec{k}}(\vec{r})=e^{-\vec{k}\cdot\vec{V}_t(\vec{r})}U_{\vec{k}}(\vec{r})\,.$$

Consequently, a Bloch theorem for crystals with structural distortions is as follows: The eigenfunction $\psi_{\vec{k}}(\vec{r})$ of the electronic Schrödinger equation of a crystal with structural distortions whose wreath group consists of the operator pairs $[\vec{V}_F(\vec{r})\| F]$ is of the form

$$\psi_{\vec{k}}(\vec{r})=e^{-i\vec{k}\cdot\vec{r}}U_{\vec{k}}(\vec{r})\,,$$

where,

$$[\vec{V}_t(\vec{r}\,')\|\mathrm{t}]\,U_{\vec{k}}(\vec{r})=e^{-\vec{k}\cdot\vec{V}_t(\vec{r})}U_{\vec{k}}(\vec{r})\,.$$

As an example of the use of this Bloch theorem for crystals with structural distortions, we consider the nearly-free-electron approximation. In this approximation $U_{\vec{k}}(\vec{r})$ is given by the Fourier integral

$$U_{\vec{k}}(\vec{r}) = \int A_{\vec{k}}(\vec{p}) e^{i\vec{p}\cdot\vec{r}}\, d\vec{p}\,. \tag{19}$$

We shall determine the nonvanishing coefficients $A_{\vec{k}}(\vec{p})$ and subsequently the form of $U_{\vec{k}}(\vec{r})$ in the case of a crystal with structural distortions. The coefficients $A_{\vec{k}}(\vec{p})$ are given by the inverse of Eq. (19)

$$A_{\vec{k}}(\vec{p}) = \int U_{\vec{k}}(\vec{r}) e^{-i\vec{p}\cdot\vec{r}}\, d\vec{r}\,.$$

Substituting $U_{\vec{k}}(\mathrm{r})$ from Eq. (18) into the above, using then Eq. (19), and summing over all elements of the subgroup $\underline{T}_w$ of the wreath group of the crystal with structural distortions, we derive an integral equation for the coefficients $A_{\vec{k}}(\vec{p})$

$$A_{\vec{k}}(\vec{p}) = \frac{1}{N} \sum_{t} \exp[i(\vec{k}-\vec{p}\,')\cdot\vec{V}_t(\vec{r}) + i(\vec{p}-\vec{p}\,')\cdot\vec{r} - i\vec{p}\,'\cdot\vec{t}\,] A_{\vec{k}}(\vec{p}\,')\, d\vec{r}\, d\vec{p}\,'\,. \tag{20}$$

We shall consider the case of a crystal with periodic structural distortions given by $\vec{D}(\vec{r}) = \vec{D}\sin\vec{Q}\cdot\vec{r}$. The crystal with these structural distortions has as its symmetry group a wreath group, a subgroup of the wreath product $\underline{V}^{-}\times_w \Omega_F$ consisting of the operator pairs $[\mathrm{V}_F(\mathrm{r}) \| F]$ where $\mathrm{V}_F(\mathrm{r})$ is defined by Eq. (9) for all atomic positions $\vec{r}$ of the crystal $C_s(3)$. We assume then that the Hamiltonian of the electronic Schrödinger Eq. (15) is invariant under a subgroup of $\underline{V}^{-}\times_w \Omega_{E_s(3)}$ consisting of operator pairs $[\vec{V}_F(\vec{r}) \| F]$ where $\vec{V}_F(\vec{r})$ is again defined by Eq. (9), but for all points of $E_s(3)$.

For this case of a crystal with these structural distortions, using Eq. (12), Eq. (20) can be rewritten as

$$A_{\vec{k}}(\vec{p}) = \sum_{m,m'} \int \left(\frac{1}{N} \sum_{\vec{t}} \exp[-i(\vec{p}\,' + m'\vec{Q})\cdot\vec{t}\,] \right) \left(\int \exp[i(m+m')\vec{Q}\cdot\vec{r} + i(\vec{p}\,'-\vec{p})\cdot\vec{r}\,]\, d\vec{r} \right)$$
$$\times A_{\vec{k}}(\vec{p}\,') J_m(\vec{D}\cdot(\vec{k}-\vec{p}\,')) J_{m'}(-\vec{D}\cdot(\vec{k}-\vec{p}\,'))\, d\vec{p}\,'\,.$$

Summing over $\vec{t}$ and integrating over $\vec{r}$ we obtain

$$A_{\vec{k}}(\vec{p}) = (2\pi)^3 \sum_{m,m'} \int J_m(\vec{D}\cdot(\vec{k}-\vec{p}\,')) J_{m'}(-\vec{D}\cdot(\vec{k}-\vec{p}\,')) A_{\vec{k}}(\vec{p}\,')\, \delta(\vec{K}-\vec{p}\,'-m\vec{Q})\, \delta(\vec{p}\,'-\vec{p}+(m+m')\vec{Q})\, d\vec{p}\,'\,,$$

where K is a reciprocal-lattice vector of the translation subgroup $\underline{T}$ of $\underline{F}$. $A_{\vec{k}}(\vec{p})$ is equal to zero if the two delta functions in the above equation are not simultaneously satisfied. It follows that $A_{\vec{k}}(\vec{p}) = 0$ if $\vec{p} \neq \vec{K} + m\vec{Q}$. Consequently, using Eq. (19), in the nearly-free-electron approximation, the eigenfunctions of a one-electron Schrödinger equation for a crystal with periodic structural distortions $\vec{D}(\vec{r}) = \vec{D}\sin\vec{Q}\cdot\vec{r}$ is given by

$$\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} \sum_{\vec{K},m} A_{\vec{k}}(\vec{K},m)\, e^{i(\vec{K}+m\vec{Q})\cdot\vec{r}}\,, \tag{21}$$

where $\vec{K}$ is a reciprocal-lattice vector of the crystal $C_s(3)$.

The charge density $\rho_{\vec{k}}(\vec{r}) = |\psi_{\vec{k}}(\vec{r})|^2$ corresponding to the $\vec{k}$th eigenfunction $\psi_{\vec{k}}(\vec{r})$ can be calculated using Eq. (21). This charge density can be written in the form

$$\rho_{\vec{k}}(\vec{r}) = \rho^{0}_{\vec{k}}(\vec{r}) + \sum_{m\neq 0} \rho^{m}_{\vec{k}}(\vec{r}) \cos(m\vec{Q}\cdot\vec{r})\,,$$

where the functions $\rho^{m}_{\vec{k}}(\vec{r})$, $m = 0, 1, \ldots,$ are functions invariant under translations of the crystal $C_s(3)$; i.e., $\rho^{m}_{\vec{k}}(\vec{r}+\vec{t}) = \rho^{m}_{\vec{k}}(\vec{r})$. Consequently, the charge density in the nearly free-electron approximation for a crystal $C_s(3)$ with periodic structural distortions is a modulated charge density, containing terms consisting of charge densities having the translational periodicity of the undistorted crystal $C_s(3)$ modulated by functions $\cos(m\vec{Q}\cdot\vec{r})$.

ACKNOWLEDGMENTS

The author would like to thank Professor W. Opechowski of the University of British Columbia for discussions. Financial support for a visit to the University of British Columbia (UBC) provided by Professor B. Bergerson and the Faculty Scholarship Support Fund—Phase II (Penn State U.), and for a visiting scientist appointment at the Technion—Israel Institute of Technology (Technion—IIT) arranged by Professor A. Ron is gratefully acknowledged.

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