Symmetry-adapted Wannier functions in perfect antiferromagnetic chromium

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In this paper Wannier functions are introduced which are symmetry adapted to the magnetic space group of perfect (or commensurate) antiferromagnetic chromium. They are defined as unitary transforms of Bloch functions belonging to paramagnetic energy bands with certain symmetry labels. It turns out that such Wannier functions can be constructed from one of the narrowest conduction bands of paramagnetic Cr. There is evidence that the existence of this band is the cause for the stability of the spin-density-wave state in Cr.

I. INTRODUCTION

In the electron theory of metals, Wannier functions[1] have proved to be a useful set of orthonormal basis functions which emphasize the atomic character of conduction electrons, particularly in narrow bands. Although their general properties are known in great detail for simple and composite bands[2–9] and though their symmetry can be determined in any space group,[10–15] they presumably have not yet reached their full potential in electron theory. As explained in the following, this statement is suggested by the individual symmetry properties of the conduction bands of metals.

In an earlier paper[16] we reported on the finding that superconductors (and *only* superconductors) possess a narrow, roughly-half-filled conduction band (called the σ band) whose Bloch functions can be unitarily transformed into optimally localized spin-dependent[17] Wannier functions which are symmetry adapted to the full space group of the considered metal. In fact, this finding suggests that the existence of localized states which are represented by such Wannier functions is necessary for the stability of the superconductive state. One may ask whether there is evidence for other physical phenomena which are connected with the existence of special localized states belonging to narrow half-filled bands.

This paper reports on a characteristic of the band structure of chromium: it is possible to transform the Bloch functions of one of the narrowest rougly-half-filled bands of Cr (called the AF band, see Fig. 1) into an orthonormal set of optimally localized Wannier functions which are symmetry adapted to the space group D_{4h}^6 of the commensurate antiferromagnetic phase of Cr. The fact that the other nonferromagnetic bcc transition metals (except for Mo), V, Nb, W, and Ta, do not possess such an AF band (or have an AF band which is far from being half filled) suggests that the existence of this special conduction band is the cause for the stability of the spin-density-wave state in Cr. There is also experimental evidence for symmetry-adapted localized states belonging to the spin-density wave: Polarized-neutron diffraction experiments performed by Stassis *et al.* show that the induced magnetic moments of the spin-density wave in Cr are of both spin and *orbital* origin.[18]

This finding on the chromium bands should be theoretically interpreted in the framework of a suitable localized model which extends (but does not contradict) the familiar concept of a spin-density-wave state as initiated by Overhauser,[19] and which is compatible with the present understanding of the commensurate-incommensurate transition in terms of special features of the Fermi surface of Cr.[20–23] In the author's opinion, such a suitable model would be the nonadiabatic Heisenberg model as presented in Ref. 16. In the framework of this model, the connection between σ bands and superconductivity can be interpreted in terms of superconductive eigenstates[16,24] in such a way that the quantitative results of the standard theory of superconductivity remain essentially unchanged.

The nonadiabatic Heisenberg model emphasizes the dualism of bandlike and atomic character of conduction electrons to a higher degree than it is possible in the framework of the adiabatic (or Born-Oppenheimer) approximation. This is because, within this model, the

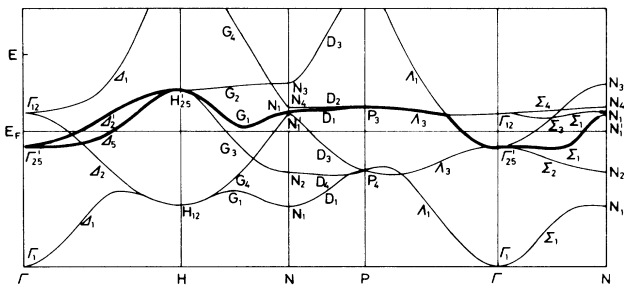

FIG. 1. Energy bands of paramagnetic Cr as estimated by Laurent *et al.* (Ref. 34). The heavy line denotes the antiferromagnetic band (AF band) whose Bloch functions can be unitarily transformed into Wannier functions being symmetry-adapted to the antiferromagnetic space group D_{4h}^6. Between Γ and H, the AF band consists of two branches corresponding to the different lines Δ (lower branch) and Λ (upper branch) in the antiferromagnetic Brillouin zone.

nonadiabatic localized functions *exactly* diagonalize the operator of Coulomb interaction [see Eq. (2.23) or (3.20) of Ref. 16] and hence have certain properties of one-electron eigenfunctions. As a consequence, the ground state of the electron system crucially depends on the symmetry properties of these localized functions. The nonadiabatic model within the form given in Ref. 16, however, cannot be simply applied to magnetic phenomena and hence a theoretical explanation of the evident connection between the AF band and the stability of a spin-density-wave state in Cr is not given in this paper.

The arrangement of the paper is as follows. In Sec. II A we give the matrix equations which determine the optimally localizable and symmetry-adapted Wannier functions derived in three former papers.[14,15,17] These equations are solvable if the symmetry labels of the considered bands fulfill certain conditions, equivalent to the conditions derived by Des Cloizeaux.[10] For simplicity we write down these equations for only two composite bands; corresponding equations with n-dimensional matrices hold for n composite bands in any space group. The formalism given in Sec. II A hence may also be used for the construction of Wannier functions symmetry adapted to other spin arrangements in other metals. In Sec. II B the matrix equations are solved for two distinct composite bands (see Fig. 2) in the space group D_{4h}^6 of antiferromagnetic Cr. In Sec. III the band structures of the nonferromagnetic bcc transition metals Cr, V, Mo, Nb, W, and Ta are examined for the existence of Wannier functions symmetry adapted to D_{4h}^6.

II. GROUP THEORY OF OPTIMALLY LOCALIZABLE WANNIER FUNCTIONS

A. General analysis

The space group G of perfect antiferromagnetic chromium is

$$G=D_{4h}^6 \tag{2.1}$$

in the usual Schönflies notation.[25] The space-group operators are denoted by $\{\alpha \mid \mathbf{t}\}$, where α is an operator of the point group G_0 of G and $\mathbf{t}$ is a translation according to

$$\{\alpha \mid \mathbf{t}\}\mathbf{r}=\alpha\mathbf{r}+\mathbf{t} \ . \tag{2.2}$$

The multiplication rule of space-group operators is

$$\{\alpha \mid \mathbf{t}\}\{\alpha' \mid \mathbf{t}'\}=\{\alpha\alpha' \mid \alpha\mathbf{t}'+\mathbf{t}\} \tag{2.3}$$

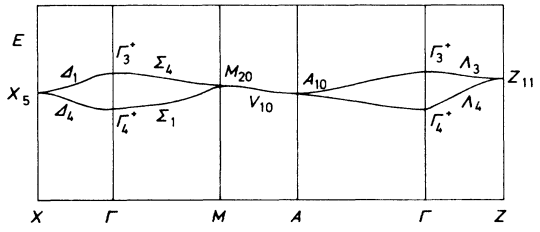

FIG. 2. Schematic plot of the first pair of energy bands in Table I.

and hence

$$\{\alpha \mid \mathbf{t}\}^{-1}=\{\alpha^{-1} \mid -\alpha^{-1}\mathbf{t}\} \tag{2.4}$$

is the inverse of $\{\alpha \mid \mathbf{t}\}$. If $f(\mathbf{r})$ is a function of position then, as usual,

$$\{\alpha \mid \mathbf{t}\}f(\mathbf{r})=f(\{\alpha \mid \mathbf{t}\}^{-1}\mathbf{r}) \ . \tag{2.5}$$

The point group G_0 is the tetragonal point group D_{4h},

$$G_0=D_{4h} \tag{2.6}$$

with the sixteen elements listed, e.g., in Eq. (1) of Ref. 25. In the group D_{4h}^6, eight elements of D_{4h}, namely the elements of the group C_{4h} (in the Schönflies notation), are, on their own, symmetry operations of the crystal[26] (cf. Sec. II of Ref. 25). The remaining operations of D_{4h} are associated with the nonprimitive translation $\tau=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ as indicated in Fig. 1 of Ref. 25. In the following, we denote by $\{\alpha \mid \tau(\alpha)\}$ an element of G with

$$\tau(\alpha)=\begin{cases}\mathbf{0} & \text{for } \alpha\in C_{4h} \ , \\ \tau & \text{for } \alpha\in D_{4h}\setminus C_{4h} \ .\end{cases} \tag{2.7}$$

The magnetic group of perfect antiferromagnetic chromium is

$$G^M=G+\{K \mid \tau\}G \tag{2.8}$$

since the time-inversion operator K is associated with the nonprimitive translation τ (cf. Fig. 1 in Ref. 25). The operator K acts on a function of position, $f(\mathbf{r})$, according to[27]

$$Kf(\mathbf{r})=f^*(\mathbf{r}) \ . \tag{2.9}$$

The magnetic point group G_0^M belonging to G^M reads as

$$G_0^M=G_0+KG_0 \ . \tag{2.10}$$

Consider the two composite bands depicted in Fig. 2 in the Brillouin zone of antiferromagnetic chromium (as given in Fig. 3 of Ref. 25), with symmetry notations which may be identified from Table II of Ref. 25. (The connection of these bands with the paramagnetic band structure of chromium will be established in Sec. III.) Assume the Bloch functions $\varphi_{\mathbf{k}',n}(\mathbf{r})$ $(n=1,2)$ of these two bands to be known within the basic domain[26] of the antiferromagnetic Brillouin zone, whose characteristic property is that it contains one and only one $\mathbf{k}$ vector of each star. (The basic domain is the small prism which is bounded by the symmetry planes $Z\Gamma MA$, ΓMX, ΓXRZ, and ZTR.) In what follows $\mathbf{k}'$ and $\mathbf{k}_s'$ denote vectors in the basic domain (e.g., vectors within or on the surface of the basic domain), and on the surface of the basic domain, respectively. From now on, the basic domain is called the first basic domain. We assume the Brillouin zone to be divided into sixteen basic domains and, as usual, $\mathbf{k}$ space to be divided into Brillouin zones with the first Brillouin zone containing the first basic domain.

If $\mathbf{k}'$ runs through all vectors in the first basic domain then $\alpha\mathbf{k}'$ (with $\alpha\in G_0$) runs through all vectors in one of the sixteen basic domains of the first Brillouin zone. Since $\{\alpha \mid \tau(\alpha)\}\varphi_{\mathbf{k}',n}(\mathbf{r})$ is a Bloch function with wave vector $\alpha\mathbf{k}'$ we assume, as usual, the Bloch functions in the

first Brillouin zone to be calculated from the given functions in the first basic domain by

$$\varphi_{\alpha\mathbf{k}',n}(\mathbf{r})=\{\alpha\mid\tau(\alpha)\}\varphi_{\mathbf{k}',n}(\mathbf{r})\quad(\alpha\in G_0)\ , \tag{2.11}$$

where $\tau(\alpha)$ is defined by Eq. (2.7). The Bloch functions in the other Brillouin zones are assumed to be given by

$$\varphi_{\mathbf{k}+\mathbf{K},n}(\mathbf{r})=\varphi_{\mathbf{k},n}(\mathbf{r})\ , \tag{2.12}$$

where $\mathbf{K}$ runs through all vectors of the reciprocal lattice. Finally, we assume $\varphi_{\mathbf{k}',n}(\mathbf{r})$ to vary smoothly (for fixed $\mathbf{r}$) within the first basic domain (such a choice of the Bloch functions is possible because of the analytic properties of the Hamiltonian operator[28]). From (2.11) and (2.12) follows that the Bloch functions also vary smoothly within the other basic domains in each Brillouin zone of $\mathbf{k}$ space. The Bloch functions defined in this way, however, will generally be discontinuous if we go from any basic domain into another adjacent basic domain (which may lie within the same or another Brillouin zone).[14]

We write the above defined Bloch functions as a vector

$$\phi_{\mathbf{k}}=\begin{pmatrix}\varphi_{\mathbf{k},1}(\mathbf{r})\\ \varphi_{\mathbf{k},2}(\mathbf{r})\end{pmatrix} \tag{2.13}$$

and set

$$\tilde{\phi}_{\mathbf{k}}=\underline{F}(\mathbf{k})\phi_{\mathbf{k}}\ . \tag{2.14}$$

The $\mathbf{k}$-dependent two-dimensional unitary matrix $\underline{F}(\mathbf{k})$ shall be chosen such that $\tilde{\phi}_{\mathbf{k}}$ is continuous in the whole $\mathbf{k}$ space. Fortunately, this demand on $\underline{F}(\mathbf{k})$, which determines this matrix partially, may be treated by group theory. From the two components of the vector $\tilde{\phi}_{\mathbf{k}}$ (which are quasi-Bloch-functions[3,8]) we will later construct Wannier functions. These are *optimally localizable* since those quasi-Bloch-functions from which the best localized Wannier functions are constructed are necessarily continuous in $\mathbf{k}$ space.[29]

Generally, and in particular for the two bands considered, $\underline{F}(\mathbf{k})$ cannot be chosen periodic in $\mathbf{k}$ space. Hence we put

$$\underline{F}(\mathbf{k}+\mathbf{K})=\underline{S}(\mathbf{K})\underline{F}(\mathbf{k})\ , \tag{2.15}$$

where $\underline{S}(\mathbf{K})$ is a (two-dimensional) unitary matrix with

$$\underline{S}(\mathbf{K}'+\mathbf{K}'')=\underline{S}(\mathbf{K}')\underline{S}(\mathbf{K}'') \tag{2.16}$$

and $\mathbf{K}$ is (still) a vector of the reciprocal lattice. We now may give the equations for $\underline{F}(\mathbf{k})$ as they have been derived in Ref. 14. Let $\phi_{\mathbf{k}}$ be given as stated above. $\tilde{\phi}_{\mathbf{k}}$ then varies smoothly in $\mathbf{k}$ space if four conditions are satisfied:

$$\underline{F}(\alpha\mathbf{k}')=\underline{D}_0^*(\alpha)e^{i\alpha\mathbf{k}'\cdot\tau(\alpha)}\underline{F}(\mathbf{k}')\quad\text{for }\alpha\in G_0 \tag{2.17}$$

and for $\alpha\mathbf{k}'\neq\mathbf{k}'$ holds in the first Brillouin zone;

$$\underline{S}(\alpha\mathbf{K}_j)=\underline{D}_0^*(\alpha)\underline{S}(\mathbf{K}_j)[\underline{D}_0^*(\alpha)]^{-1}e^{i\alpha\mathbf{K}_j\cdot\tau(\alpha)}\quad\text{for }\alpha\in G_0 \tag{2.18}$$

holds for the fundamental vectors $\mathbf{K}_x$, $\mathbf{K}_y$, and $\mathbf{K}_z$ of the reciprocal lattice;

$$\underline{D}^*_{\mathbf{k}'_s}(\{\alpha\mid\tau(\alpha)\})=[\underline{F}(\mathbf{k}'_s)]^{-1}\underline{D}_0^*(\alpha)\underline{F}(\mathbf{k}'_s)e^{i\mathbf{k}'_s\cdot\tau(\alpha)}\quad\text{for }\alpha\in G_{0\mathbf{k}'_s} \tag{2.19}$$

holds at any point $\mathbf{k}'_s$ on the surface of the first basic domain which is an interior point of the first Brillouin zone;

$$\underline{D}^*_{\mathbf{k}'_s}(\{\alpha\mid\tau(\alpha)\})=[\underline{F}(\mathbf{k}'_s)]^{-1}\underline{S}(\mathbf{K}_{\mathbf{k}'_s}(\alpha))\underline{D}_0^*(\alpha)\underline{F}(\mathbf{k}'_s)e^{i\alpha\mathbf{k}'_s\cdot\tau(\alpha)}\quad\text{for }\alpha\in G_{0\mathbf{k}'_s} \tag{2.20}$$

holds at any point $\mathbf{k}'_s$ lying on both the surface of the first basic domain and the surface of the first Brillouin zone. $G_{\mathbf{k}'_s}$ and $G_{0\mathbf{k}'_s}$ denote the little group at point $\mathbf{k}'_s$ and its point group, respectively.[30] $\underline{D}_0(\alpha)$ and $\underline{D}_{\mathbf{k}'_s}(\{\alpha\mid\tau(\alpha)\})$ are the matrix representatives of $\{\alpha\mid\tau(\alpha)\}$ in the representations $R_{\mathbf{k}'_s}$ at points Γ and $\mathbf{k}'_s$, respectively, to which $\phi_{\mathbf{k}'_s}$ (2.13) belongs. At point Γ one has $R_0=\Gamma_3^+\oplus\Gamma_4^+$, and at point M, e.g., $R_M=M_{20}$ (cf. Fig. 2). The vector $\mathbf{K}_{\mathbf{k}'_s}(\alpha)$ of the reciprocal lattice is defined by

$$\mathbf{K}_{\mathbf{k}'_s}(\alpha)=\mathbf{k}'_s-\alpha\mathbf{k}'_s\ . \tag{2.20'}$$

The form of $\underline{F}(\mathbf{k})$ as expressed by (2.17) and (2.19) ensures that the Wannier functions will be symmetry adapted to the space group G. If we demand that they are adapted to the full magnetic group G^M (2.8), $\underline{F}(\mathbf{k})$ and $\underline{S}(\mathbf{K})$ must follow two additional equations:[31]

$$\underline{D}^*_{\mathbf{k}'}(\{KI\mid\tau\})=[\underline{F}(\mathbf{k}')]^{-1}\underline{D}_0^*(KI)\underline{F}^*(\mathbf{k}')e^{i\mathbf{k}'\cdot\tau} \tag{2.21}$$

must hold at each point $\mathbf{k}'$ in the first basic domain and

$$\underline{S}(\mathbf{K}_j)=\underline{D}_0^*(KI)\underline{S}^*(\mathbf{K}_j)[\underline{D}_0^*(KI)]^{-1}e^{i\mathbf{K}_j\cdot\tau} \tag{2.22}$$

must hold [besides (2.18)] for the fundamental vectors $\mathbf{K}_x$, $\mathbf{K}_y$, and $\mathbf{K}_z$ of the reciprocal lattice [cf. Eqs. (7.1) and (11.21) of Ref. 17; in (11.21) $\mathbf{K}_{\bar{\gamma}}=\mathbf{0}$ according to (11.9)]. $\underline{D}_0(KI)$ is the matrix representative of the product of the time-inversion operator K with the inversion I in the corepresentation[26] of G_0^M (2.10) derived from $R_0=\Gamma_3^+\oplus\Gamma_4^+$, and $\underline{D}_{\mathbf{k}'}(\{KI\mid\tau\})$ is the matrix representative of $\{KI\mid\tau\}=\{K\mid\tau\}\{I\mid\mathbf{0}\}$ in the corepresentation derived from the small representation $R_{\mathbf{k}'}$ at point $\mathbf{k}'$.

We now ask under which conditions the above equations for $\underline{F}(\mathbf{k})$ are solvable. The following statements hold for all (composite) bands which satisfy the compatibility relations if we go from any point $\mathbf{k}'_s$ to a point in its neighborhood. The first equation (2.17) states how $\underline{F}(\mathbf{k})$ in the first Brillouin zone must be calculated from $\underline{F}(\mathbf{k}')$ and hence is trivially solvable. In Eq. (2.19) the matrices

$$\check{\underline{D}}_{\mathbf{k}'_s}(\{\alpha\mid\tau(\alpha)\})=\underline{D}_0(\alpha)e^{-i\mathbf{k}'_s\cdot\tau(\alpha)} \tag{2.23}$$

get unitarily transformed by $\underline{F}^*(\mathbf{k}'_s)$ into the matrices

$\underline{D}_{\mathbf{k}'_s}(\{\alpha \mid \tau(\alpha)\})$. Since in this equation $\mathbf{k}'_s$ denotes an interior point of the Brillouin zone the matrices (2.23) form, for $\alpha = \in G_{0\mathbf{k}'_s}$, a small representation $\check{R}_{\mathbf{k}'_s}$ of $G_{\mathbf{k}'_s}$.[27] For $\mathbf{k}'_s \to \mathbf{0}$, both $\check{R}_{\mathbf{k}'_s}$ and $R_{\mathbf{k}'_s}$ are compatible with $R_0 = \Gamma_3^+ + \Gamma_4^+$. Consequently, $\check{R}_{\mathbf{k}'_s}$ and $R_{\mathbf{k}'_s}$ are equivalent and hence Eq. (2.19) is solvable.

In Eq. (2.20) the matrices

$$\hat{\underline{D}}_{\mathbf{k}'_s}(\{\alpha \mid \tau(\alpha)\}) = \underline{S}^*(\mathbf{K}_{\mathbf{k}'_s}(\alpha))\underline{D}_0(\alpha)e^{-i\alpha\mathbf{k}'_s\cdot\tau(\alpha)} \tag{2.24}$$

get unitarily transformed by $\underline{F}^*(\mathbf{k}'_s)$ into $\underline{D}_{\mathbf{k}'_s}(\{\alpha \mid \tau(\alpha)\})$ at points $\mathbf{k}'_s$ on the surface of the Brillouin zone. As shown in Ref. 14, the matrices (2.24) form a small (or allowed[27]) representation $\hat{R}_{\mathbf{k}'_s}$ of $G_{\mathbf{k}'_s}$ if and only if $\underline{S}(\mathbf{K})$ obeys Eq. (2.18). Equation (2.20) is hence solvable if, in addition to (2.18), $\underline{S}(\mathbf{K})$ may be chosen such that $\hat{R}_{\mathbf{k}'_s}$ is equivalent to $R_{\mathbf{k}'_s}$,

$$\hat{R}_{\mathbf{k}'_s} \equiv R_{\mathbf{k}'_s} \ . \tag{2.25}$$

This condition, which is equivalent to Eq. (34) of Ref. 10, often cannot be fulfilled and hence, in these cases, optimally localizable Wannier functions cannot be constructed. We will find, however, suitable matrices $\underline{S}(\mathbf{K})$ for the composite bands depicted in Fig. 2.

At points $\mathbf{k}'_s$ on the surface of the first basic domain, Eq. (2.21) together with (2.19) or (2.20) is an equivalence transformation of corepresentations (which also contain antiunitary elements). Two corepresentations are equivalent if they are derived[26] from equivalent representations. At interior points $\mathbf{k}'_s$ of the Brillouin zone $\underline{D}_0(KI)e^{-i\mathbf{k}'\cdot\tau}$ and $\underline{D}_{\mathbf{k}'_s}(\{KI \mid \tau\})$ belong to the corepresentations derived from the equivalent representations $\check{R}_{\mathbf{k}'_s}$ (2.23) and $R_{\mathbf{k}'_s}$, respectively, and hence (2.21) together with (2.19) is solvable. At points $\mathbf{k}'_s$ on the surface of the Brillouin zone, $\underline{D}_0(KI)e^{-i\mathbf{k}'\cdot\tau}$ is matrix representative of $\{KI \mid \tau\}$ in the corepresentation derived from $\hat{R}_{\mathbf{k}'_s}$ (2.24) if and only if $\underline{S}(\mathbf{K})$ obeys Eq. (2.22) [in addition to (2.18)].[17] Eq. (2.21) together with (2.20) is hence solvable if and only if (2.22) and (2.25) is fulfilled.

We summarize as follows. Equations (2.17) and (2.19) together with (2.21) are solvable; (2.20) together with (2.21) is solvable if and only if matrices $\underline{S}(\mathbf{K})$ (2.16) can be found which satisfy (2.18), (2.22), and (2.25). The task to find such matrices $\underline{S}(\mathbf{K})$ gets considerably simplified by a theorem which, in another form, was proven by Des Cloizeaux:[10] $\hat{R}_{\mathbf{k}'_s}$ is equivalent to $R_{\mathbf{k}'_s}$ at each point $\mathbf{k}'_s$ on the surface of the Brillouin zone if these representations are equivalent at each point of maximum symmetry[32] on the surface of the Brillouin zone.[14] Because of this theorem, which is a consequence of the compatibility relations, we need only examine (2.25) at the points M, X, R, Z, and A in the Brillouin zone of antiferromagnetic Cr.

B. Symmetry-adapted Wannier functions

We determine the matrices $\underline{S}(\mathbf{K})$ for the two composite bands depicted in Fig. 2 and consider first Eqs. (2.18) and (2.22) and the four operators $\{C_{4z}^+ \mid \mathbf{0}\}$, $\{I \mid \mathbf{0}\}$, $\{C_{2x} \mid \tau\}$, and $\{KI \mid \tau\}$ of the magnetic space group. (The notation of the point-group elements is given in Ref. 26 and in Sec. II of Ref. 25.) In the representation $R_0 = \Gamma_3^+ + \Gamma_4^+$ on has $\underline{D}_0(KI) = \underline{D}_0(I) = \left(\begin{smallmatrix}1&0\\0&1\end{smallmatrix}\right)$, $\underline{D}_0(C_{4z}^+) = \left(\begin{smallmatrix}-1&0\\0&-1\end{smallmatrix}\right)$, and $\underline{D}_0(C_{2x}) = \left(\begin{smallmatrix}1&0\\0&-1\end{smallmatrix}\right)$.[26] With these matrices and $e^{i\mathbf{K}_j\cdot\tau} = -1$ $(j = x,y,z)$ we get from (2.18) and (2.22) twelve (in some cases equivalent) equations having the general solution

$$\underline{S}(\mathbf{K}_x) = \underline{S}(\mathbf{K}_y) = \pm \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}$$

and (2.26)

$$\underline{S}(\mathbf{K}_z) = \pm \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} .$$

For the other operators of the magnetic group we do not get new equations from (2.18) and (2.22).

Now consider point A of the antiferromagnetic Brillouin zone (as given in Fig. 3 of Ref. 25) and condition (2.25). According to (2.24) the matrix representative of the operator $\{S_{4z}^+ \mid \mathbf{0}\}$ in the representation $\hat{R}_A$ is

$$\hat{\underline{D}}_A(\{S_{4z}^+ \mid \mathbf{0}\}) = \underline{S}^*(\mathbf{K}_x + \mathbf{K}_z) \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \tag{2.27}$$

since

$$\mathbf{K}_A(S_{4z}^+) = \mathbf{K}_x + \mathbf{K}_z$$

[cf. Eq. (2.20′)] and

$$\underline{D}_0(S_{4z}^+) = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} .$$

The matrix representative of $\{S_{4z}^+ \mid \mathbf{0}\}$ in the representation $R_A = A_{10}$ also is

$$\underline{D}_A(\{S_{4z}^+ \mid \mathbf{0}\}) = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \tag{2.28}$$

as given in Table II(c) of Ref. 25. Both matrices (2.27) and (2.28) are equivalent (in the present case even equal) if

$$\underline{S}(\mathbf{K}_x + \mathbf{K}_z) = \underline{\mathbb{1}} \ . \tag{2.29}$$

This gives with (2.26) and (2.16)

$$\underline{S}(\mathbf{K}_x) = \underline{S}(\mathbf{K}_y) = \underline{S}(\mathbf{K}_z) = \pm \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} . \tag{2.30}$$

The minus in this equation may be omited since the matrices with the minus sign are equivalent to those with the plus sign. In the same way it may be shown that the matrix representatives of the other two generating elements of G_A (see Table II(c) of Ref. 25) in the representation $\hat{R}_A$ [with $\underline{S}(\mathbf{K})$ as given in (2.30)] may be transformed into those in the representation A_{10} each time by the same ma-

trix. Thus, at point A, (2.25) is true and hence Eqs. (2.20) and (2.21) are solvable; their solution is

$$\underline{F}(A)=\frac{1}{\sqrt{2}}\begin{bmatrix} i & -1 \\ 1 & -i \end{bmatrix} \tag{2.31}$$

since [in Eq. (2.21)]

$$\underline{D}_A(\{KI\mid\tau\})=\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{2.32}$$

and

$$\underline{D}_0(KI)=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{2.33}$$

as derived from Eq. (7.3.45) in Ref. 26.

The matrices $\underline{S}(\mathbf{K})$ now are completely determined by (2.30). Consequently, the small representation $\hat{R}_{\mathbf{k}_s'}$ (2.24) at the other points of maximum symmetry are also fixed. In the same way as shown for point A we find that at points X, M, Z, and R, Eq. (2.25) is true if the considered bands are labeled by X_5, M_{20}, Z_{11}, and R_5, respectively, as indicated in Fig. 2.

With (2.30) all equations determining $\underline{F}(\mathbf{k})$ are solvable and hence the two components of $\bar{\phi}_{\mathbf{k}}$ can be assumed to vary smoothly through $\mathbf{k}$ space. They are, however, not yet appropriate for the construction of Wannier functions with well-defined local symmetry centers since the matrices $\underline{S}(\mathbf{K})$ are not diagonal. Because of (2.16) all $\underline{S}(\mathbf{K})$ commute and hence all of them can be diagonalized by the same matrix $\underline{M}$,

$$\bar{\underline{S}}(\mathbf{K})=\underline{M}\,\underline{S}(\mathbf{K})\underline{M}^{-1}\,, \tag{2.34}$$

and further the diagonal matrices $\bar{\underline{S}}(\mathbf{K})$ have the form

$$\bar{\underline{S}}(\mathbf{K})=\begin{bmatrix} e^{i\mathbf{K}\cdot\boldsymbol{\rho}_1} & 0 \\ 0 & e^{i\mathbf{K}\cdot\boldsymbol{\rho}_2} \end{bmatrix}. \tag{2.35}$$

Equation (2.30) gives, with

$$\underline{M}=\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & i \\ 1 & -i \end{bmatrix}, \tag{2.36}$$

$$\boldsymbol{\rho}_1=\mathbf{0} \tag{2.37}$$

and

$$\boldsymbol{\rho}_2=\boldsymbol{\tau}\,.$$

$\underline{S}(\mathbf{K})$ may be replaced by $\bar{\underline{S}}(\mathbf{K})$ if in Eqs. (2.15), and (2.17)–(2.22) the matrices $\underline{D}_0(\alpha)$, $\underline{D}_0(KI)$, and $\underline{F}(\mathbf{k})$ are replaced by

$$\bar{\underline{D}}_0(\alpha)=\underline{M}^*\underline{D}_0(\alpha)(\underline{M}^*)^{-1}\,, \tag{2.38}$$

$$\bar{\underline{D}}_0(KI)=\underline{M}^*\underline{D}_0(KI)\underline{M}^{-1}\,, \tag{2.39}$$

$$\bar{\underline{F}}(\mathbf{k})=\underline{M}\,\underline{F}(\mathbf{k})\,, \tag{2.40}$$

respectively.

The two components $\bar{\bar{\varphi}}_{\mathbf{k},n}(\mathbf{r})$ $(n=1,2)$ of

$$\bar{\bar{\phi}}_{\mathbf{k}}=\bar{\underline{F}}(\mathbf{k})\phi_{\mathbf{k}} \tag{2.41}$$

now are appropriate for the construction of Wannier functions. According to Eqs. (2.15) and (2.37) the functions $\bar{\bar{\varphi}}_{\mathbf{k},1}(\mathbf{r})$ and $e^{-i\mathbf{k}\cdot\boldsymbol{\tau}}\bar{\bar{\varphi}}_{\mathbf{k},2}$ are periodic in $\mathbf{k}$ space and hence we can define Wannier functions, as usual,

$$w_1(\mathbf{r}-\mathbf{R})=\frac{1}{\sqrt{N}}\sum_{j,\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}}[\bar{F}(\mathbf{k})]_{1j}\varphi_{\mathbf{k},j}(\mathbf{r}) \tag{2.42}$$

and

$$w_2(\mathbf{r}-\mathbf{R}-\boldsymbol{\tau})=\frac{1}{\sqrt{N}}\sum_{j,\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau})}[\bar{F}(\mathbf{k})]_{2j}\varphi_{\mathbf{k},j}(\mathbf{r}) \tag{2.43}$$

with $\mathbf{k}$ running through the N vectors of the antiferromagnetic Brillouin zone and $j=1,2$. $\mathbf{R}$ denotes a lattice point of the primitive tetragonal lattice labeled in Fig. 1 of Ref. 25 by the, say, spin-up direction.

The symmetry of the Wannier functions is determined by Eqs. (2.17), (2.19), and (2.21). The lengthy derivation, which is given in Ref. 15 for the space group operators and in Ref. 17 for the time inversion, results in

$$w_i(\alpha^{-1}(\mathbf{r}-\mathbf{R}-\boldsymbol{\rho}_i))=\sum_{j=1}^{2}[\bar{D}_0(\alpha)]_{ji}w_j(\mathbf{r}-\mathbf{R}-\boldsymbol{\rho}_i)\quad\text{for }\alpha\in G_0 \tag{2.44}$$

and

$$Kw_i(\mathbf{r}-\mathbf{R}-\boldsymbol{\rho}_i)=\sum_{j=1}^{2}[\bar{D}_0(K)]_{ji}w_j(\mathbf{r}-\mathbf{R}-\boldsymbol{\rho}_i)\,. \tag{2.45}$$

These equations show that the vectors $\boldsymbol{\rho}_i$ (2.37) denote the symmetry centers of the Wannier functions. Equations (2.38) and (2.39) give with (2.36)

$$\bar{\underline{D}}_0(\alpha)=\begin{cases} d(\alpha)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \text{for }\alpha\in C_{4h}, \\ d(\alpha)\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} & \text{for }\alpha\in D_{4h}\setminus C_{4h}\,, \end{cases} \tag{2.46}$$

and

$$\bar{\underline{D}}_0(K)=\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{2.47}$$

where

$$d(\alpha)=\begin{cases} 1 & \text{for }\alpha=E,\ I,\ C_{2x},\ C_{2y},\ C_{2z},\ \sigma_x,\ \sigma_y,\ \text{and }\sigma_z, \\ -1 & \text{for }\alpha=C_{4z}^{\pm},\ S_{4z}^{\pm},\ C_{2a},\ C_{2b},\ \sigma_{da},\ \text{and }\sigma_{db}\,. \end{cases} \tag{2.48}$$

Equation (2.47) follows from (2.33) since $\bar{\underline{D}}_0(KI)=\bar{\underline{D}}_0(K)\bar{\underline{D}}_0^*(I)$ and $\bar{\underline{D}}_0(I)=\underline{1}$. With (2.47) and (2.9) Eq. (2.45) simply reads as

$$w_1^*(\mathbf{r})=w_2(\mathbf{r}) \tag{2.49}$$

and hence, with (2.46), Eq. (2.44) becomes

$$w(\alpha^{-1}\mathbf{r}) = \begin{cases} d(\alpha)w(\mathbf{r}) & \text{for } \alpha \in C_{4h}, \\ d(\alpha)w^*(\mathbf{r}) & \text{for } \alpha \in D_{4h} \setminus C_{4h} \end{cases} . \quad (2.50)$$

The functions $w(\mathbf{r}-\mathbf{R})$ and $w^*(\mathbf{r}-\mathbf{R}-\tau)$ form an orthonormal set of basis functions for the considered bands (Fig. 2) and are situated at the atoms with spin-down and spin-up direction, respectively. They belong to a one-dimensional representation of the group C_{4h} (which is the group of their symmetry centers $\mathbf{R}$ and $\mathbf{R}+\tau$, respectively) and hence have the most simple symmetry which localized functions may have in antiferromagnetic chromium. Thus, the two composite bands in Fig. 2 are "simple bands" and "class-I bands" in the notation of Kohn[3] and Zak[33], respectively, having uniquely defined Wannier functions. In this paper, their uniqueness is expressed by the fact that the matrices $\underline{S}(\mathbf{K})$ are, according to (2.30), completely determined for the optimally localizable Wannier functions.

III. ANTIFERROMAGNETIC WANNIER FUNCTIONS IN BCC TRANSITION METALS

Wannier functions which are symmetry adapted to the perfect antiferromagnetic state of chromium exist if $\underline{S}(\mathbf{K})$ follows Eq. (2.30). The four types of composite bands (in the space group D_{4h}^6) with such matrices $\underline{S}(\mathbf{K})$ are listed in Table I. By means of Table I in Ref. 25 it may be established whether or not the Bloch functions of a given *paramagnetic* band can be transformed such that they form, in the antiferromagnetic state, one of the bands listed in Table I.

Consider, e.g., the band structure of paramagnetic Cr (Ref. 34) depicted in Fig. 1, in particular the band denoted by the heavy line. It is labeled by the representations

$$\Gamma_{25}', H_{25}', N_1, P_3, \Delta_5, \text{ and } \Delta_2' .$$

If the symmetry is restricted to the antiferromagnetic space group D_{4h}^6, we get, according to Table I in Ref. 25,

$$\begin{aligned} &\Gamma_{25}' \to \Gamma_4^+ + \Gamma_5^+, \quad H_{25}' \to \Gamma_3^+ + \Gamma_5^+, \quad P_3 \to A_{10} + A_{11} , \\ &N_1 \to M_{20}, \quad N_1 \to R_5, \quad \Delta_5 \to X_5 + X_{10}, \quad \Delta_2' \to Z_{11} . \end{aligned} \quad (3.1)$$

The paramagnetic Bloch functions of this band may hence be transformed such that they form basis functions for the small representations labeling the bands depicted in Fig. 2 (and given in the first row of Table I). Consequently, from the Bloch functions of this paramagnetic band we may construct optimally localizable Wannier functions (2.50) which are symmetry adapted to the antiferromagnetic state. (In this context, it is meaningless that, in the paramagnetic band structure, the considered band is connected to other bands since these connections disappear when any small antiferromagnetic perturbation is activated.) Any paramagnetic band which is compatible with one of the bands listed in Table I, e.g., the Cr band denoted in Fig. 1, we call antiferromagnetic band (AF band).

Between the points Γ and N, the AF band of Cr "jumps" from the lower to the upper Σ_1 band. This is allowed since both bands have the same symmetry and the jump does not cross the Fermi level (see, for a detailed consideration, Sec. 4.1 of Ref. 17). However, the jump should be very small (compared with the bandwidth) since it impairs the localization of the Wannier functions.

The antiferromagnetic band of Cr is one of the narrowest bands of Laurent *et al.*[34] (Fig 1) which is roughly half-filled. These findings are confirmed by further published band structures of paramagnetic Cr.[21,35–39] (In the band structure of Kulikov *et al.*[39] the state N_1 has about the threefold distance from the Fermi level as the state N_1' and hence the jump between Γ and N has the order of magnitude of the half bandwidth. In this case, the Wannier functions will be badly localized. In the band structures as estimated by Asano and Yamashita[21] and Rath and Callaway,[36] on the other hand, the state N_1 lies between the state N_1' and the Fermi level. For this position of N_1 the jump does not exist and hence the Wannier functions will be best localized.)

Among the other nonferromagnetic bcc transition metals V, Nb, Mo, Ta, and W there is only Mo (Ref. 40) having a narrow roughly half-filled AF band. (We notice that the positions of the states N_1 or N_4 is decisive for an AF band since only the states N_2', N_3', N_1, and N_4 are compatible with M_{10} or M_{20} (see Table I of Ref. 25 and Table I) and N_2' or N_3' does not occur in d-band groups.) In the band structures of Nb and Ta (Ref. 41) the AF band is nearly empty; in the band structure of W (Refs. 42 and 43) the jump between Γ and N tends to be markedly greater as for Cr; V (Ref. 37) has an AF band which is far from being half-filled. Summarizing we state that, as to the existence of a narrow half-filled AF band, Cr and Mo evidently have a special position among the bcc transition metals.

IV. RESULTS

We have determined all pairs of energy bands in the Brillouin zone of perfect antiferromagnetic Cr (or of any antiferromagnetic metal with the space group D_{4h}^6) whose Bloch functions may be unitarily transformed into Wannier functions which are symmetry adapted to D_{4h}^6 and which have one Wannier function at each atom. These

TABLE I. Symmetry labels of all the pairs of energy bands in the Brillouin zone of antiferromagnetic Cr which have at each atom one symmetry-adapted Wannier function. For the symmetry notations see Table II of Ref. 25.

Γ_3^+, Γ_4^+	X_5	M_{20}	A_{10}	Z_{11}	R_5
Γ_3^-, Γ_4^-	X_{10}	M_{10}	A_{11}	Z_{11}	R_{10}
Γ_1^+, Γ_2^+	X_5	M_{20}	A_{11}	Z_{10}	R_5
Γ_1^-, Γ_2^-	X_{10}	M_{10}	A_{10}	Z_{10}	R_{10}

pairs of energy bands are listed in Table I (and the two bands in the first row of Table I are depicted in more detail in Fig. 2). By means of Table I of Ref. 25 it may be established whether or not the symmetry of the Bloch functions of a given *paramagnetic* band is compatible with the symmetry of one of the band pairs listed in Table I (see Sec. III). This is the case for the energy band of paramagnetic Cr denoted in Fig. 1 by the heavy line. Consequently, the Bloch functions of this band, shortly called AF band, may be unitarily transformed into Wannier functions being symmetry adapted to the commensurate antiferromagnetic phase of Cr.

Among the other nonferromagnetic bcc transition metals, Cr has a special position: the metals Nb, V, W, and Ta do not possess an AF band or it is in these metals far from being half-filled (the only exception is the superconductor Mo which has a band structure very similar to Cr). This evident connection between the existence of a narrow AF band and the stability of a spin-density-wave state together with the evident connection between narrow σ bands and the stability of superconductive states (as established on eighteen metals[16]) suggest that the symmetry (and spin dependence) of the Wannier functions which belong to the narrowest half-filled energy bands of a metal determines the physical properties of the conduction electrons in a similar way as the symmetry of the valence-electron orbitals determines the physical and chemical properties of an atom.

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[1]G. H. Wannier, Phys. Rev. **52**, 191 (1937).
[2]J. C. Slater, Massachusetts Institute of Technology, Technical Report No. 4, 1953 (unpublished).
[3]W. Kohn, Phys. Rev. B **7**, 4388 (1973).
[4]J. C. Slater, Phys. Rev. **87**, 807 (1952).
[5]G. F. Koster, Phys. Rev. **89**, 67 (1953).
[6]E. I. Blount, Solid State Phys. **13**, 334 (1962).
[7]H. Teichler, Phys. Status Solidi B **43**, 307 (1971).
[8]B. Lix, Phys. Status Solidi B **44**, 411 (1971).
[9]H. Bross, Z. Phys. **243**, 311 (1971).
[10]J. Des Cloizeaux, Phys. Rev. **129**, 554 (1963).
[11]J. Des Cloizeaux, Phys. Rev. **135**, A685 (1964).
[12]J. Des Cloizeaux, Phys. Rev. **135**, A698 (1964).
[13]J. Zak, Phys. Rev. Lett. **47**, 450 (1981).
[14]E. Krüger, Phys. Status Solidi B **52**, 215 (1972).
[15]E. Krüger, Phys. Status Solidi B **52**, 519 (1972).
[16]E. Krüger, Phys. Rev. B **30**, 2621 (1984).
[17]E. Krüger, Phys. Status Solidi B **61**, 193 (1974).
[18]C. Stassis, G. R. Kline, and S. K. Sinha, Phys. Rev. B **11**, 2171 (1975).
[19]A. W. Overhauser, Phys. Rev. Lett. **4**, 462 (1960); A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).
[20]W. M. Lomer, Proc. Phys. Soc. London **80**, 489 (1962).
[21]S. Asano and J. Yamashita, J. Phys. Soc. Jpn. **23**, 714 (1967).
[22]K. Machida, Phys. Rev. B **30**, 418 (1984).
[23]K. Machida and M. Fujita, Phys. Rev. B **30**, 5284 (1984).
[24]E. Krüger (unpublished).
[25]E. Krüger, Phys. Rev. B **32**, 7493 (1985).
[26]C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Claredon, Oxford, 1972).
[27]H.-W. Streitwolf, *Gruppentheorie in der Festkörperphysik* (Akademische Verlagsgesellschaft Geest & Portig KG, Leipzig, 1967).
[28]L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).
[29]D. S. Bulyanitsa and Yu. E. Svetlow, Fiz. Tverd. Tela (Leningrad) **4**, 1339 (1962) [Soviet Phys.—Solid State **4**, 981 (1962).
[30]$G_{\mathbf{k}}$ and $G_{0\mathbf{k}}$ contain the elements $\{\alpha \mid t\}$ and α of the space group G and the point group G_0, respectively, with $\alpha\mathbf{k}=\mathbf{k}+\mathbf{K}$, where $\mathbf{K}$ denotes a vector of the reciprocal lattice.
[31]If not $K \in G_0^M$ and $I \in G_0^M$ then the Eqs. (2.21) and (2.22) must be replaced by Eqs. (11.21) and (7.1) of Ref. 17.
[32]In the book of Bradley and Cracknell (Ref. 26) the points of maximum symmetry are called "points of symmetry."
[33]J. Zak, Phys. Rev. Lett. **54**, 1075 (1985).
[34]D. G. Laurent, J. Callaway, J. L. Fry, and N. E. Brener, Phys. Rev. B **23**, 4977 (1981).
[35]J. Kübler, J. Magn. Magn. Mater. **20**, 277 (1980).
[36]J. Rath and J. Callaway, Phys. Rev. B **8**, 5398 (1973).
[37]M. Yasui, E. Hayashi, and M. Shimizu, J. Phys. Soc. Jpn. **29**, 1446 (1970).
[38]N. I. Kulikov, Sov. J. Low Temp. Phys. **5**, 173 (1979).
[39]N. I. Kulikov and E. T. Kulatov, J. Phys. F **12**, 2291 (1982).
[40]R. J. Iverson and L. Hodges, Phys. Rev. B **8**, 1429 (1973).
[41]L. F. Mattheiss, Phys. Rev. B **1**, 373 (1969).
[42]L. F. Mattheiss, Phys. Rev. **139**, A1893 (1965).
[43]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **29**, 5372 (1984).