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Superconducting Pair States for Transition Metals in the Atomic Representation

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This paper is a sequel to one by Appel and Kohn, in which the theory of superconductivity was cast into the Wannier (or atomic) representation. This representation should be especially useful for narrow-band superconductors. In the present paper, group theoretical methods are used to show how to construct appropriately symmetrized pair states in this atomic representation. Specific applications to s and d bands in bcc and fcc lattices, and to d bands in β-tungsten structures are worked out.

I. INTRODUCTION

In an earlier paper[1] (hereafter referred to as I) we have cast the theory of superconductivity in narrow energy bands into the atomic (or Wannier) representation in order to highlight the atomic nature of the electrons responsible for the superconducting transition. In particular, the homogeneous vertex equation (really a system of coupled equations), which defines the transition temperature $kT_c = \beta^{-1}$, was derived for a Bravais lattice [I(2.23) and (2.27)]; the nature of the irreducible interaction in the site representation was discussed; and the vertex equation was solved in the so-called contact approximation (I, Sec. III), in which the paired electrons are taken to be on the same atomic site.

Our eventual hope is for quantitative calculations of transition temperatures in real narrow-band superconductors and our first model calculations were far from that goal. In the present paper we take a further necessary step by solving the group-theoretical problem which arises when the paired electrons occupy different lattice sites. We also extend our earlier work to metals in which the crystal structure has a basis, as, for example, the important β-tungsten structures. The necessity for a group-theoretical reduction is evident from the nature of the coupled vertex equations. For a crystal structure with basis it has the form

$$\Gamma(f, \omega) = -\frac{1}{\beta} \sum_{f'} \sum_{\omega'} \Gamma(f', \omega') \langle f', \omega' | \mathcal{K} | f, \omega \rangle , \tag{1.1}$$

where f and f' describe states in which the paired electrons occupy particular sites and orbitals, $\mathcal{K}$ is a kernel incorporating the electron-electron interaction, and ω, ω' are imaginary frequencies [cf. I (2.23)]. Now consider, for example, the d electrons in Nb_3Sn. Let us restrict the paired electrons to occupying either the same site or nearest-neighbor sites, probably an adequate model. Then even after the translational and permutation groups have been taken care of, there are still 240 distinct f labels, which clearly demonstrates the compelling need for all possible reductions by symmetry considerations. In fact, in this example such considerations reduce the system of Eq. (1.1) to the system

$$\Gamma(\eta, \omega) = -\frac{1}{\beta} \sum_{\eta'} \sum_{\omega'} \Gamma(\eta', \omega') \langle \eta' \omega' | K | \eta \omega \rangle , \tag{1.2}$$

with only ten independent labels η; it is still a formidable but perhaps not insuperable problem.

The present paper is devoted to the construction of the symmetrized pair states

$$|\eta\rangle = f\rangle\langle f|\eta\rangle \tag{1.3}$$

and the corresponding new kernel K. The general theory for an arbitrary crystal structure is given in Secs. II and III. Specific applications to s- and d-like orbitals in bcc and fcc lattices are worked out in Sec. IV and to d electrons in the β-tungsten structure in Sec. V.

II. GENERAL FORMULATION OF PROBLEM

In Eq. (1.1) we have written down the homogeneous vertex equation for a general crystal structure. Since in the remainder of this paper we shall only deal with spatial symmetries, we shall suppress the frequencies ω and ω'. Also, unless otherwise stated, summation over repeated indices will be implied. Thus we rewrite Eq. (1.1) in the form

$$\Gamma(f) = -\frac{1}{\beta}\,\Gamma(f')\langle f'|\mathcal{K}|f\rangle\ . \qquad (2.1)$$

Here, f denotes an electron pair state:

$$f \equiv (\vec{\mathrm{n}}_1,\ \vec{\tau}_1,\ i_1(\vec{\tau}_1);\ \vec{\mathrm{n}}_2,\ \vec{\tau}_2,\ i_2(\vec{\tau}_2))\ , \qquad (2.2)$$

where the $\vec{\mathrm{n}}_l$ label the unit cells,[2] the $\vec{\tau}_\alpha$ are atomic positions within the unit cells, and $i_\alpha(\vec{\tau}_\alpha)$ are the Wannier orbitals associated with the site $\vec{\tau}_\alpha$.

By an obvious generalization of [I (2.23)], the kernel $\mathcal{K}$ is given by

$$\begin{aligned}\langle f'|\mathcal{K}|f\rangle = \langle f'\omega'|\mathcal{K}|f\omega\rangle = {} & G(\vec{\mathrm{n}}_1',\ \vec{\tau}_1',i_1'(\vec{\tau}_1'),\omega';\ \vec{\mathrm{n}}_1'',\vec{\tau}_1'',\ i_1''(\vec{\tau}_1''),\omega'')G(\vec{\mathrm{n}}_2',\ \vec{\tau}_2',\ i_2'(\vec{\tau}_2'),-\omega';\ \vec{\mathrm{n}}_2'',\vec{\tau}_2'',\ i_2''(\vec{\tau}_2''),-\omega'') \\ & \times\langle \vec{\mathrm{n}}_1'',\ \vec{\tau}_1'',\ i_1''(\vec{\tau}_1''),\ \omega'';\ \vec{\mathrm{n}}_2'',\ \vec{\tau}_2'',\ i_2''(\vec{\tau}_2''),\ -\omega''\,|I|\,\vec{\mathrm{n}}_1,\ \vec{\tau}_1,\ i_1(\vec{\tau}_1),\ \omega;\ \vec{\mathrm{n}}_2,\ \vec{\tau}_2,\ i_2(\vec{\tau}_2),\ -\omega\rangle,\end{aligned} \qquad (2.3)$$

where the G's are electron Green's functions in the Wannier representation and I is the irreducible interaction between the pair of electrons.

Now denote the permutation group by $\mathcal{P}$ (elements P), the space group of the crystal by $\mathcal{G}$ (elements G), and their direct product by

$$\mathcal{Q} \equiv \mathcal{G}\times\mathcal{P} \quad \text{(elements } Q\text{)}\ . \qquad (2.4)$$

Then the kernel $\mathcal{K}$ must be invariant under the operations of the group $\mathcal{Q}$, i.e.,

$$\langle Qf'|\mathcal{K}|Qf\rangle = \langle f'|\mathcal{K}|f\rangle\ . \qquad (2.5)$$

Therefore the solutions $\Gamma(f)$ of Eq. (2.1) must belong to irreducible representations of $\mathcal{Q}$, which we label by the index j. Now the spatial electron-pair states are symmetric under permutation since the spin function in a singlet and hence antisymmetric. Furthermore, according to available experimental evidence, the superconducting state has the same invariance properties under the operations of the space group $\mathcal{G}$ as the crystal structure itself (i.e., there is no broken space-group symmetry). Thus the physically relevant solution of Eq. (2.1) must be invariant under the operations of the full group $\mathcal{Q}$:

$$\Gamma(Qf) = \Gamma(f) \quad (\text{all } Q \text{ and } f)\ , \qquad (2.6)$$

that is, it must belong to the identity representation $j = 1$. This symmetry property greatly reduces the number of independent unknowns and equations in the system of Eq. (2.1)

We now follow standard procedures and introduce the complete set of pair states $|j\gamma\rangle$ which transform according to the irreducible representations j of the group $\mathcal{Q}$; $\gamma = 1, 2, \ldots$ labels the different states corresponding to the same j. We write

$$|j\gamma\rangle = |f\rangle\langle f|j\gamma\rangle \qquad (2.7)$$

and define

$$\Gamma(j\gamma) \equiv \Gamma(f)\langle f|j\gamma\rangle\ . \qquad (2.8)$$

Then Eq. (2.1) becomes, in the $|j\gamma\rangle$ representation,

$$\begin{aligned}\Gamma(j\gamma) &= -\frac{1}{\beta}\,\Gamma(j'\gamma')\langle j'\gamma'|\mathcal{K}|j\gamma\rangle \\ &= -\frac{1}{\beta}\,\Gamma(j\gamma')\langle j\gamma'|\mathcal{K}|j\gamma\rangle \quad (\text{not summed over } j)\end{aligned} \qquad (2.9)$$

since, in view of the symmetry property (2.5), $\mathcal{K}$ does not couple different representations j. We are only interested in states belonging to the identity representation $j = 1$. Hence, we write

$$|\gamma\rangle \equiv |1\gamma\rangle,\quad \Gamma(\gamma) \equiv \Gamma(1\gamma)\ , \qquad (2.10)$$

and

$$\langle\gamma'|\mathcal{K}|\gamma\rangle \equiv \langle 1\gamma'|\mathcal{K}|1\gamma\rangle = \langle\gamma'|f'\rangle\langle f'|\mathcal{K}|f\rangle\langle f|\gamma\rangle\ . \qquad (2.11)$$

Equation (2.9) now takes the form

$$\Gamma(\gamma) = -\frac{1}{\beta}\,\Gamma(\gamma')\langle\gamma'|\mathcal{K}|\gamma\rangle\ . \qquad (2.12)$$

The corresponding $\Gamma(f)$ satisfy, by construction, the symmetry condition (2.6).

The problem of solving the vertex equation, and thus determining the transition temperature, can then be broken into three steps:

(i) Calculate the matrix elements $\langle f'|\mathcal{K}|f\rangle$ [Eq. (2.3)] of the kernel $\mathcal{K}$ in the Wannier representation $|f\rangle$.

(ii) Determine (in a convenient form) the transformation matrices $\langle f|\gamma\rangle$ or, equivalently, the "symmetrized" pair states

$$|\gamma\rangle = |f\rangle\langle f|\gamma\rangle\ , \qquad (2.13)$$

invariant under the full group $\mathcal{Q}$,

$$Q|\gamma\rangle = |\gamma\rangle , \qquad (2.14)$$

which are needed for the construction of the kernel $\langle\gamma'|\mathcal{K}|\gamma\rangle$ according to Eq. (2.11).

(iii) Solve the set of coupled equations (2.1). In the present paper we deal with step (ii).

III. CONSTRUCTION OF SYMMETRIZED PAIR STATES AND CORRESPONDING KERNEL

Let $|f\rangle$ be any initial pair state in the sense of Eq. (2.2). Then, as is well known,[3] the state

$$|\gamma\rangle = \text{const} \times \textstyle\sum_\nu Q_\nu |f\rangle , \qquad (3.1)$$

where ν runs over all group elements of $\mathcal{Q}$ and is invariant in the sense of (2.14). This follows immediately from the rearrangement theorem:

$$Q \textstyle\sum_\nu Q_\nu = \sum_\nu Q_\nu . \qquad (3.2)$$

The constant in (3.1) and similar constants below are for normalization purposes.

It follows also from the rearrangement theorem (3.2) that if $|f^{(1)}\rangle$ and $|f^{(2)}\rangle$ are too "equivalent" states, in the sense of

$$|f^{(1)}\rangle = Q|f^{(2)}\rangle , \qquad (3.3)$$

they give rise, via (3.1), to the same invariant state $|\gamma\rangle$. Thus we may restrict ourselves to inequivalent starting states $|f\rangle$.

A. Disposition of Translational and Permutation Symmetries

It is now convenient to replace the cell indices $\vec{n}_1$ and $\vec{n}_2$ by the two vectors

$$\vec{m} \equiv \text{cell index of the center of mass} , \quad \tfrac{1}{2}(\vec{n}_1 + \vec{\tau}_1 + \vec{n}_2 + \vec{\tau}_2) \qquad (3.4)$$

$$\vec{n} \equiv \vec{n}_1 - \vec{n}_2 , \qquad (3.5)$$

and to write the basic pair states in the form

$$|f\rangle \equiv |\vec{m} g\rangle , \qquad (3.6)$$

where

$$g \equiv (\vec{n};\ \vec{\tau}_1,\ i(\vec{\tau}_1);\ \vec{\tau}_2,\ i(\vec{\tau}_2)) \qquad (3.7)$$

[see Eq. (2.2)]. All $\vec{m}$ vectors assigned to the center of mass of the pair must be unambiguous, even if the center of mass falls on a cell boundary (see Ref. 2). Now the primitive translation elements $T_{\vec{m}}$ of the space group have the effect

$$T_{\vec{m}}|\vec{0} g\rangle = |\vec{m} g\rangle . \qquad (3.8)$$

Hence, for purposes of constructing the invariant states $|\gamma\rangle$, we may restrict ourselves to states with $\vec{m} = \vec{0}$.

Next, since $\vec{m}$ is invariant under the operations E and P of the permutation group, we define the normalized states

$$|\vec{m} s(f)\rangle \equiv \text{const}(|\vec{m} g\rangle + P|\vec{m} g\rangle) . \qquad (3.9)$$

Then the totally symmetric state generated from $|f\rangle$ is

$$|\gamma\rangle = \text{const} \times \textstyle\sum_\nu G_\nu |\vec{0} s\rangle , \qquad (3.10)$$

where ν runs over all elements of the space group.

It is useful to extract explicitly the subgroup of primitive translations from (3.10). For this purpose we introduce the set $\bar{G}_\alpha$ of all elements of the space group $\mathcal{G}$, which take a given state $|\vec{0} s\rangle$ into another state $|\vec{0} s'\rangle$, with $\vec{m}$ still equal to $\vec{0}$. Then every element G can be written uniquely as a product

$$G = T\bar{G} , \qquad (3.11)$$

where T is a fundamental translation vector. Hence

$$\textstyle\sum_\nu G_\nu = (\sum_{\vec{m}} T_{\vec{m}})(\sum_\alpha \bar{G}_\alpha) . \qquad (3.12)$$

This leads us to define, for each initial state $|f\rangle$, the normalized "cell state"

$$|\vec{0}\eta\rangle \equiv \text{const} \times \textstyle\sum_\alpha \bar{G}_\alpha |\vec{0} s\rangle , \qquad (3.13)$$

in which the center-of-mass cell index $\vec{m} = \vec{0}$, and the corresponding translated state

$$|\vec{m}\eta\rangle = T_{\vec{m}}|\vec{0}\eta\rangle . \qquad (3.14)$$

Clearly, since

$$\langle f'|f\rangle = 0 , \qquad (3.15)$$

unless $\vec{n}'_l = \vec{n}_l$ ($l = 1$ and 2) and hence $\vec{m}' = \vec{m}$, it follows that

$$\langle \vec{m}'\eta|\vec{m}\eta\rangle = \delta_{\vec{m}',\vec{m}} . \qquad (3.16)$$

Therefore, the normalized state $|\gamma\rangle$ is given by

$$|\gamma\rangle = \frac{1}{N^{1/2}} \sum_{\vec{m}} |\vec{m}\eta\rangle = \frac{1}{N^{1/2}} \Big(\sum_{\vec{m}} T_{\vec{m}}\Big)|\vec{0}\eta\rangle , \qquad (3.17)$$

where N is the number of unit cells. Clearly, there is a one-to-one correspondence between the states $|\gamma\rangle$ and $|\eta\rangle$, so that we may write

$$\eta = \eta(\gamma) \quad \text{or} \quad \gamma = \gamma(\eta). \qquad (3.18)$$

Our next objective is to determine a kernel K such that

$$\langle\gamma'|\mathcal{K}|\gamma\rangle = \langle\vec{0}\eta'|K|\vec{0}\eta\rangle = \langle\eta'|K|\eta\rangle , \qquad (3.19)$$

where for brevity we write

$$|\eta\rangle \equiv |\vec{0}\eta\rangle . \qquad (3.20)$$

This desired kernel connects only cell states with $\vec{m} = \vec{0}$.

First, we take care of permutation symmetry by defining the symmetrized kernel $\mathcal{K}^s$ as follows:

$$\langle f'|\mathcal{K}^s|f\rangle = \tfrac{1}{2}(\langle f'|\mathcal{K}|f\rangle + \langle Pf'|\mathcal{K}|f\rangle) \qquad (3.21)$$

[symmetrization with respect to f is superfluous in view of Eq. (2.5)]. Then, clearly, in working with the symmetrized states $|\vec{m} s\rangle$, $|\vec{m}\eta\rangle$, and

$|\gamma\rangle$, $\mathcal{K}^s$ is equivlaent to $\mathcal{K}$. Further, the kernel $\mathcal{K}^s$ (like $\mathcal{K}$) has the full translational invariance of the crystal. Therefore,

$$\langle\gamma'|\mathcal{K}|\gamma\rangle=\langle\gamma'|\mathcal{K}^s|\gamma\rangle=\frac{1}{N}\sum_{\vec{m},\vec{m}'}\langle\vec{m}'\eta'|\mathcal{K}^s|\vec{m}\eta\rangle$$
$$=\sum_{\vec{m}'}\langle\vec{m}'\eta'|\mathcal{K}^s|\vec{0}\eta\rangle. \qquad (3.22)$$

We now define the contracted kernel K by the equation

$$\langle\eta'|K|\eta\rangle\equiv\textstyle\sum_{\vec{m}}\langle\vec{m}'\eta'|\mathcal{K}^s|\vec{0}\eta\rangle \qquad (3.23)$$

[cf. I (2.28)]; in the sense of Eq. (3.18) we write

$$\Gamma(\gamma)=\Gamma(\gamma(\eta))=\Gamma(\eta). \qquad (3.24)$$

Then Eq. (2.1) assumes the form

$$\Gamma(\eta)=-(1/\beta)\Gamma(\eta')\langle\eta'|K|\eta\rangle. \qquad (3.25)$$

The new kernel is given, in virtue of Eq. (3.23), by

$$\langle\eta'|K|\eta\rangle=\textstyle\sum_{\vec{m}'}\langle\vec{m}'\eta'|\vec{m}'g'\rangle\langle\vec{m}'g'|\mathcal{K}^s|\vec{0}g\rangle\langle\vec{0}g|\vec{0}\eta\rangle$$
$$=\langle\vec{0}\eta'|\vec{0}g'\rangle\textstyle\sum_{\vec{m}'}\langle\vec{m}'g'|\mathcal{K}^s|\vec{0}g\rangle\langle\vec{0}g|\vec{0}\eta\rangle. \qquad (3.26)$$

Thus, assuming that we have calculated the kernel $\mathcal{K}^s$ in the f [or $(\vec{m}g)$] representation, we now must construct the cell states

$$|\eta\rangle\equiv|\vec{0}\eta\rangle=|\vec{0}g'\rangle\langle\vec{0}g'|\vec{0}\eta\rangle. \qquad (3.27)$$

B. Practical Construction of Cell States $|\eta\rangle$

We have seen that, starting from an arbitrary pair state $|f\rangle=|\vec{m}g\rangle$, the cell state $|\eta\rangle$ is obtained by symmetrizing between the two electrons, translating so that $\vec{m}$ becomes $\vec{0}$, which leads to the state $|\vec{0}s\rangle$ [Eq. (3.9)], and finally operating with the sum of the elements $\overline{G}_\alpha$, which were defined following Eq. (3.10):

$$|\eta\rangle=|\vec{0}\eta\rangle=\text{const}\times\textstyle\sum_\alpha\overline{G}_\alpha|\vec{0}s\rangle. \qquad (3.28)$$

For practical purposes it is convenient to break down further the last step. In the state $|\vec{0}s\rangle$, a particular pair of atomic sites $(\vec{v}_1^{(1)},\ \vec{v}_2^{(1)})$, where $\vec{v}\equiv\vec{n}+\tau$, with $\vec{m}=\vec{0}$, is occupied. In general, there may exist other pairs of sites, $(\vec{v}_1^{(\lambda)},\ \vec{v}_2^{(\lambda)})$, where $\lambda=1,\ 2,\ldots,\lambda_0$, also with $\vec{m}=\vec{0}$, which arise from the first pair by operation of the space group $\mathcal{G}$ [we consider $(\vec{v}_1,\vec{v}_2)\equiv(\vec{v}_2,\vec{v}_1)$]. Now denote the subgroup of $\mathcal{G}$ which leaves the pair of sites $(\vec{v}_1^{(1)},\vec{v}_2^{(1)})$ invariant by $\mathcal{S}$ (elements S_τ); and let $\overline{\overline{G}}_\lambda$ be any *one* element of $\mathcal{G}$ which takes the pair $(\vec{v}_1^{(1)},\vec{v}_2^{(1)})$ into $(\vec{v}_1^{(\lambda)},\vec{v}_2^{(\lambda)})$. Then, clearly,

$$\sum_\alpha\overline{G}_\alpha=\left(\sum_{\lambda=1}^{\lambda_0}\overline{\overline{G}}_\lambda\right)\left(\sum_\tau S_\tau\right). \qquad (3.29)$$

Hence,

$$|\eta\rangle=\text{const}\times\sum_{\lambda=1}^{\lambda_0}\overline{\overline{G}}_\lambda|\vec{0}p^{(1)}\rangle=\frac{1}{\lambda_0^{1/2}}\sum_1^{\lambda_0}|\vec{0}p^{(\lambda)}\rangle, \qquad (3.30)$$

where the normalized state

$$|\vec{0}p^{(1)}\rangle\equiv\text{const}\times\textstyle\sum_\tau S_\tau|\vec{0}s\rangle \qquad (3.31)$$

is a pair state located on atoms $(\vec{v}_1^{(1)},\vec{v}_2^{(1)})$ and invariant under all operations of the subgroup $\mathcal{S}$ and where

$$|\vec{0}p^{(\lambda)}\rangle\equiv\overline{\overline{G}}_\lambda|\vec{0}p^{(1)}\rangle. \qquad (3.32)$$

As we shall see in Secs. IV and V, one can use standard methods, such as are common in atomic and molecular physics, to construct directly the pair state $|\vec{0}p^{(1)}\rangle$, associated with two definite atomic sites and invariant under the group $\mathcal{S}$, and then, by Eq. (3.30), the full cell function $|\eta\rangle$.

IV. CELL STATES FOR bcc AND fcc METALS

We now construct the cell states $|\eta\rangle$ for the bcc and fcc structures in which many of the d- and f-band metals crystallize. These are Bravais structures with only a single atom in each unit cell. Thus the contact cell states are constructed from Wannier orbitals at one atom. The nearest-neighbor cell states involve Wannier orbitals at pairs of atoms separated by d, the nearest-neighbor distance. The truncation of the kernel [Eq. (2.3)], given by ignoring atomic distances larger than d, appears justified for d electrons (at least when their Wannier orbitals are chosen as localized as possible). For s electrons the restriction to these cell states is a poorer approximation. However, in most transition metals the s-s and s-d pairing interactions play a less important role for T_c than the d-d interaction because of a large d-electron density of states at the Fermi surface.

The valence electron configuration of transition-metal atoms has a characteristic form. For example, the Sc series has the form $4d^\mu s^\nu$, where the number of d electrons μ lies between 1 (Sc) and 10 (Pd) and where the number of s electrons ν is 1 or 2. The electron band structure of these metals, arising from this valence electron configuration, is characterized by five rather narrow d subbands overlapping and hybridizing with a wide s-p band.

A. Lattice

We take atom 1 to be located at the origin. The six Wannier orbitals centered on this atom and the irreducible representations[4] of the cubic point group O_h, according to which they transform under the symmetry operations, are given by

$$\begin{aligned}
&w_0=\varphi(\vec{r}), && \Gamma_1\\
&w_1=(15/4\pi)^{1/2}\,yzf(\vec{r}), && \Gamma_{25}'\\
&w_2=(15/4\pi)^{1/2}\,zxf(\vec{r}), && \Gamma_{25}'\\
&w_3=(15/4\pi)^{1/2}\,xyf(\vec{r}), && \Gamma_{25}'\\
&w_4=(15/16\pi)^{1/2}\,(x^2-y^2)\,g(\vec{r}), && \Gamma_{12}\\
&w_5=(15/16\pi)^{1/2}\,(2z^2-x^2-y^2)\,g(\vec{r}), && \Gamma_{12}.
\end{aligned} \qquad (4.1)$$

These functions are normalized:

$$\int w_i^2 d^3r = 1 \ . \qquad (4.2)$$

The functions φ, f, and g have cubic symmetry.

1. *Contact Cell States*

These states $|\eta\rangle$ are readily obtained from the w_i's. We observe that the symmetrized pair orbitals formed from the w_i's transform under the symmetry operations of O_h according to the symmetric direct product

$$(\Gamma_1 + \Gamma'_{25} + \Gamma_{12}) \times (\Gamma_1 + \Gamma'_{25} + \Gamma_{12})_{\mathrm{sym}} \ . \qquad (4.3)$$

This product contains the identity representation Γ_1 three times. The corresponding three pair states are already the required cell states.

We shall use the following notation:

$|ij\rangle \equiv$ pair state in which the orbitals w_i and w_j centered at atom 1 are occupied. (4.4)

Then the contact cell states are given by

$$|\eta_0\rangle = |00\rangle ,$$
$$|\eta_1\rangle = (1/\sqrt{3}\,)\,(|11\rangle + |22\rangle + |33\rangle) , \qquad (4.5)$$
$$|\eta_2\rangle = (1/\sqrt{2}\,)\,(|44\rangle + |55\rangle) \ .$$

2. *Nearest-Neighbor Cell States*

Next we construct the cell states arising from two electrons on nearest-neighbor atoms. Here the first step is to find the pair states $|\vec{0}p\rangle$ which yield the cell states $|\eta\rangle$ [Eq. (3.30)]. We consider atoms 1 and 2 in Fig. 1. The symmetry operations which leave *both* atoms invariant form the group C_{3v}. They are E (identity), $2C_3$ (rotations by $\frac{2}{3}\pi$ and $\frac{4}{3}\pi$ around the axis 1-2), $3\sigma_v$ (three reflections in planes making 120° angles with one another and intersecting along 1-2). The subgroup $\mathcal{S}$, defined below Eq. (3.28), consists here of these elements and the additional elements generated by σ_h, a reflection plane perpendicular to C_3 and through the midpoint of 1-2. Thus $\mathcal{S} = \{E,\ 2C_3,\ 3\sigma_v,\ \sigma_h,\ 2\sigma_h C_3,\ 3\sigma_h\sigma_v\}$.

To find the states $|\vec{0}p\rangle$ we proceed in this manner: First we construct Wannier orbitals that transform according to the representations of C_{3v}; next, these orbitals are used to form pair orbitals with the symmetry of C_{3v}; and, finally, these pair orbitals are symmetrized with respect to σ_h.

The orbitals on atom 1 and the representations of C_{3v} according to which they transform are given by

$$\begin{array}{ll} v_0 = w_0 \ , & \Lambda_1 \\ v_1 = (1/\sqrt{3}\,)\,(w_1 + w_2 + w_3) \ , & \Lambda_1 \\ v_2 = \sqrt{\tfrac{2}{3}}\,[w_1 - \tfrac{1}{2}(w_2 + w_3)] \ , & \Lambda_3 \\ v_3 = (1/\sqrt{2}\,)\,(w_2 - w_3) \ , & \Lambda_3 \\ v_4 = w_4 \ , & \Lambda_3 \\ v_5 = w_5 \ , & \Lambda_3 \ . \end{array} \qquad (4.6)$$

These v_i were found from the w_i with a procedure given, e.g., by Slater,[5] and using the compatibility relations between O_h and C_{3v}: $\Gamma_1 \to \Lambda_1$; $\Gamma'_{25} \to \Lambda_1, \Lambda_3$; $\Gamma_{12} \to \Lambda_3$.

The pair orbitals which we want are invariant under the group $\mathcal{S}$. They are given by those parts of the direct product

$$(2\Lambda_1 + 2\Lambda_3) \times (2\Lambda_1 + 2\Lambda_3) \qquad (4.7)$$

which transform according to the identity representation Λ_1 under C_{3v} and are invariant under σ_h. There are six such states. For pair states describing two electrons on nearest-neighbor atoms 1 and 2 we use the notation

$|ij\rangle \equiv$ pair state in which the orbitals v_i on atom 1 and v_j on atom 2 are occupied. (4.8)

Then we have the required pair states

$$|\vec{0}p_0\rangle = |00\rangle ,$$
$$|\vec{0}p_1\rangle = |11\rangle ,$$
$$|\vec{0}p_2\rangle = (1/\sqrt{2}\,)\,(|22\rangle + |33\rangle) ,$$
$$|\vec{0}p_3\rangle = (1/\sqrt{2}\,)\,(|44\rangle + |55\rangle) , \qquad (4.9)$$
$$|\vec{0}p_4\rangle = \tfrac{1}{2}\,(|24\rangle + |35\rangle + |42\rangle + |53\rangle) ,$$
$$|\vec{0}p_5\rangle = (1/\sqrt{2})\,(|10\rangle + |01\rangle) \ .$$

To construct the cell state $|\eta_i\rangle$ from the pair state $|\vec{0}p_i^{(1)}\rangle \equiv |\vec{0}p_i\rangle$, we apply to $|\vec{0}p_i^{(1)}\rangle$ the symmetry operations $\overline{\overline{G}}_\lambda$ which send this state into the states $|\vec{0}p_i^{(\lambda)}\rangle$ belonging to the same unit cell:

$$|\eta_i\rangle = \frac{1}{2}\sum_{\lambda=1}^{4} \overline{\overline{G}}_\lambda |\vec{0}p_i^{(1)}\rangle \quad (i = 0, 1, \ldots, 6) \ . \qquad (4.10)$$

In the present case the $\overline{\overline{G}}_\lambda$ may be chosen to be the four rotations of the crystal which send a point (x, y, z) into (x, y, z), $(x, -z, y)$, $(x, -y, -z)$, $(x, z, -y)$.

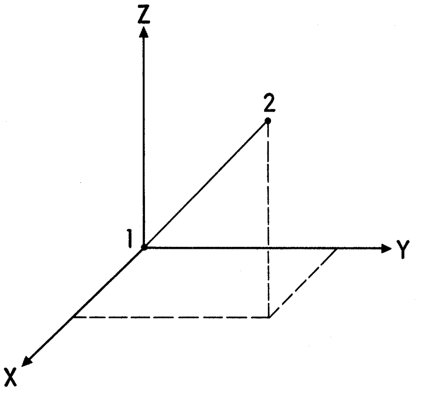

FIG. 1. Pair of next-nearest neighbors in a bcc lattice. Atom 2 has the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; a is a lattice constant.

B. fcc Lattice

The Wannier orbitals are of the same form as in the bcc case and are given by Eq. (4.1).

The contact cell states are also of the same form as for the bcc lattice [Eq. (4.5)].

The geometry of two nearest-neighbor atoms is shown in Fig. 2. The symmetry operations leaving both atoms invariant are given by the group C_{2v}. The elements are E (identity), C_2 (rotation by π around the axis 1-2), σ_v (reflection in x-y plane), σ_v' (reflection in plane $x=y$). Hence the subgroup $\mathcal{S}=\{E,\ C_2,\ \sigma_v,\ \sigma_v',\ \sigma_h,\ \sigma_h C_2,\ \sigma_h\sigma_v,\ \sigma_h\sigma_v'\}$. To find the cell states, we proceed as in the bcc case.

The orbitals on atom 1 and the associated representations of C_{2v} are given by

$$\begin{aligned}
v_0 &= w_0\,, && \Sigma_1\\
v_1 &= (1/\sqrt{2}\,)\,(w_1+w_2)\,, && \Sigma_3\\
v_2 &= (1/\sqrt{2}\,)\,(w_1-w_2)\,, && \Sigma_2\\
v_3 &= w_3\,, && \Sigma_1\\
v_4 &= w_4\,, && \Sigma_4\\
v_5 &= w_5\,, && \Sigma_1\,.
\end{aligned} \tag{4.11}$$

We have used the following compatibility relations between O_h and C_{2v}: $\Gamma_1\to\Sigma_1$; $\Gamma_{25}'\to\Sigma_1,\Sigma_2,\Sigma_3$; $\Gamma_{12}\to\Sigma_1,\Sigma_4$.

The pair orbitals of interest are invariant under the group $\mathcal{S}$. They are given by those parts of the direct product

$$(3\Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4)\times(3\Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4) \tag{4.12}$$

which transform according to the identity representation Σ_1 under C_{2v} and are invariant under σ_h. There are nine such states. They have the following form:

$$\begin{aligned}
|\vec{0}p_i\rangle &= |ii\rangle\,,\quad i=0-5\\
|\vec{0}p_6\rangle &= (1/\sqrt{2}\,)\,(|35\rangle+|53\rangle)\,,\\
|\vec{0}p_7\rangle &= (1/\sqrt{2}\,)\,(|30\rangle+|03\rangle)\,,\\
|\vec{0}p_8\rangle &= (1/\sqrt{2}\,)\,(|50\rangle+|05\rangle)\,,
\end{aligned} \tag{4.13}$$

where we have used the convention (4.8).

The nine cell states $|\eta_i\rangle$ are readily constructed from the nine states (4.13). To a state $|\vec{0}p_i^{(1)}\rangle \equiv |\vec{0}p_i\rangle$ we apply the six symmetry operations $\overline{\overline{G}}_\lambda$ which send this state into one of the six states $|\vec{0}p_i^{(\lambda)}\rangle$ [Eq. (3.32)] belonging to the same unit cell. The operations $\overline{\overline{G}}_1-\overline{\overline{G}}_6$ send a point (x, y, z) into (x, y, z), $(x, -z, y)$, $(x, -y, -z)$, $(x, z, -y)$, (y, z, x), $(y, -z, -x)$.

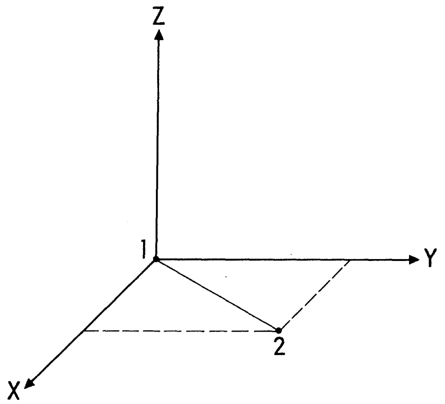

FIG. 2. Pair of nearest-neighbor atoms in a fcc lattice. Atom 2 has the position $(a/\sqrt{2},\ a/\sqrt{2},\ 0)$.

V. CELL STATES FOR β-TUNGSTEN STRUCTURES

Here we shall construct cell studies for a lattice with a basis. We choose as an example the β-tungsten lattice with space group O_h^3 since several compounds with (relatively) high values of T_c crystallize in this structure, Nb_3Sn and Nb_3Al among others. These compounds have the form A_3B and their cubic unit cell, of cube edge a, is shown in Fig. 3. The B atoms occupy the sites of a bcc lattice; the A atoms form three mutually orthogonal chains. For a given A atom the two nearest neighbors lie in the same chain at distance $\frac{1}{2}a$. The eight next-nearest neighbors lie in different chains at distance $1.22a/2$.

In constructing the cell states $|\eta\,|$, we restrict ourselves to the Wannier orbitals of the d electrons at the A sites and neglect all s and p orbitals. The pairing interaction between these d electrons is dominant because of the large d-electron density of states at the Fermi surface.[6,7]

The symmetry of a Wannier orbital w_i at an A site, e.g., site 1, is determined by the symmetry group of an A site. This group consists of all those elements of the space group which transform an A site into itself. It is isomorphic to a point group, consisting of proper and improper rotations. The symmetry group of the A atom at site 1 has the following elements (see Fig. 4): E (identity), C_2 (rotation by π around z' axis), $2\sigma_d'$ (reflections in x'-y' and y'-z' planes), $2C_2'$ (rotations by π around two orthogonal axes both perpendicular to the z' axis and tilted by ± 45° with respect to the x' axis $2\overline{S}_4'$ (nonprimitive translation by $\frac{1}{2}a$ along the z' axis, rotation by $\pm\frac{1}{2}\pi$ around the z' axis, and reflection in the x'-y' plane). The isomorphic point group is D_{2d}. In terms of its irreducible representations, the Wannier orbitals at site 1 are given by

$$\begin{aligned}
w_1 &= (5/16\pi)^{1/2}\,(3\zeta_1^2-\rho_1^2)\,h(\rho_1)\,, && W_1\\
w_2 &= (15/4\pi)^{1/2}\,\xi_1\zeta_1\,h(\vec{\rho}_1)\,, && W_3\\
w_3 &= (15/4\pi)^{1/2}\,\eta_1\zeta_1\,h(\vec{\rho}_1)\,, && W_3\\
w_4 &= (15/16\pi)^{1/2}\,(\xi_1^2-\eta_1^2)\,h(\vec{\rho}_1)\,, && W_2\\
w_5 &= (15/4\pi)^{1/2}\,\xi_1\eta_1\,h(\vec{\rho}_1)\,, && W_1\,.
\end{aligned} \tag{5.1}$$

Here $\vec{\rho}_1=\vec{r}-\vec{\tau}_1$.

The contact cell states $|\eta_1\rangle$ are easily found. The

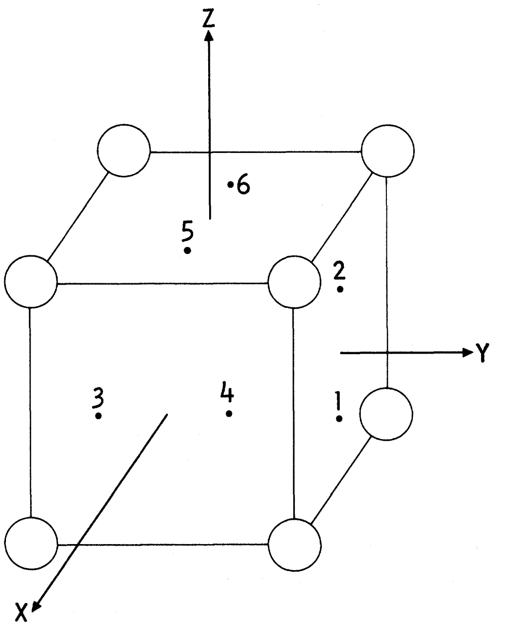

FIG. 3. Unit cell of the β-tungsten structure with the six A atoms (small circles) belonging to the unit cell. There are six other A atoms (not shown) located on the other cube faces which belong to neighboring unit cells. The B atoms (large circles) occupy the center and the corners of the cube.

pair orbitals constructed from the w_1 transform according to

$$(W_1+W_3+W_2+W_1')\times(W_1+W_3+W_2+W_1')_{\text{sym}} \,. \tag{5.2}$$

This direct product contains W_1 four times. We introduce contact pair states in the same sense as in Eq. (4.4). Then we have

$$\begin{aligned}
|\vec{0}p_1\rangle &= |11\rangle \,, \\
|\vec{0}p_2\rangle &= \sqrt{\tfrac{1}{2}}\,(|22\rangle + |33\rangle) \,, \\
|\vec{0}p_3\rangle &= |44\rangle \,, \\
|\vec{0}p_4\rangle &= |55\rangle \,.
\end{aligned} \tag{5.3}$$

In terms of these states, the four contact cell states $|\eta_i\rangle$ are given by Eq. (3.30). The six symmetry operations $\overline{\overline{G}}_\lambda$ send the point (x,y,z) into (x,y,z), $(x,y,-z)$, (y,z,x), $(y,z,-x)$, (z,x,y) and $(z,x,-y)$.

Next we determine the nearest-neighbor cell states. From Fig. 4 it is seen that the symmetry operations which leave *both* atoms 1 and 2 invariant form the group C_{2v}. The subgroup $\mathcal{S}=\{E, C_2, \sigma_v, \sigma_v', \sigma_h, \sigma_h C_2, \sigma_h\sigma_v, \sigma_h\sigma_{v'}\}$. In terms of the representations of C_{2v} the Wannier orbitals on site 1 are

$$\begin{aligned}
w_1 &: \Sigma_1 \,, \\
w_2 &: \Sigma_3 \,, \\
w_3 &: \Sigma_4 \,, \\
w_4 &: \Sigma_1 \,, \\
w_5 &: \Sigma_2 \,.
\end{aligned} \tag{5.4}$$

The compatibility relations between D_{2d} and C_{2v} which were used here are $W\to\Sigma_1$; $W_3\to\Sigma_3$, Σ_4; $W_2\to\Sigma_1$, and $W_1'\to\Sigma_2$.

For the Wannier orbitals on site 2, we introduce the appropriate relative coordinates $\vec{\rho}_2=\vec{r}-\vec{\tau}_2$. The Wannier orbitals on site 2 are denoted as $\tilde{w}_i(\vec{\rho}_2)$. These orbitals can be obtained from those on site 1 by reflection in the x-y plane:

$$\tilde{w}_i(\xi_2, \eta_2, \zeta_2) = w_i(\xi_2, \eta_2, -\zeta_2) \,. \tag{5.5}$$

The $\tilde{w}_i$ transform in the same manner as the w_i under the operations of the group C_{2v}.

The pair orbitals we want are invariant under the group $\mathcal{S}$. They are given by those parts of the direct product

$$(2\Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4)\times(2\Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4) \tag{5.6}$$

which transform according to Σ_1 under the operations of C_{2v} and are invariant under σ_h. The corresponding six nearest-neighbor pair states are given by

$$\begin{aligned}
|\vec{0}p_i\rangle &= |i\tilde{i}\rangle \,, \quad i=1-5 \\
|\vec{0}p_6\rangle &= \sqrt{\tfrac{1}{2}}\,(|1\tilde{4}\rangle + |4\tilde{1}\rangle) \,.
\end{aligned} \tag{5.7}$$

With these states $|\vec{0}p_i\rangle$, the nearest-neighbor cell states $|\eta_i\rangle$ are given by (3.30). The six symmetry operations $\overline{\overline{G}}_\lambda$ are defined in the following manner: $\overline{\overline{G}}_1$, $\overline{\overline{G}}_2$, $\overline{\overline{G}}_3$ transfer the pair 1-2 into itself and

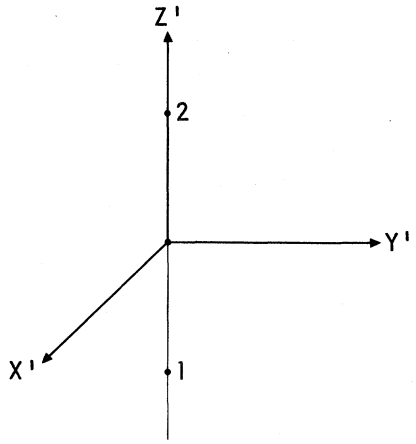

FIG. 4. Coordinate system in which the symmetry group of an A atom at site 1 is defined.

into the pairs 3-4 and 5-6, respectively. $\bar{\bar{G}}_4$, $\bar{\bar{G}}_5$, $\bar{\bar{G}}_6$ transfer these three pairs by $\frac{1}{2}a$ in z, x, and y directions, and then rotate their contours by 45° around their respective chain axis.

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Effect of Nonmagnetic Localized States in Al Films with Enhanced T_c

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Mixtures of Al with 10 wt% Al_2O_3 and various concentrations of transition-metal elements (Cr, Mn, Fe) were sputtered at 77 °K and their transition temperature (T_c) was measured without warming above 77 °K. The transition temperature (T_{c0}) of the reference Al–10-wt%-Al_2O_3 mixture is approximately 3 °K. In agreement with Kaiser's theory, T_c depends exponentially on the transition-metal concentration. The excellent agreement between film data and bulk data provides further proof that many electronic properties, in particular the density of states, of the aluminum with enhanced T_c are very close to bulk values.

The effect of nonmagnetic localized impurities such as Cr, Mn, and Fe in Al with enhanced T_c has been studied as a function of the impurity concentration. The technique used (getter-sputtering films at 77 °K) has extended the range of concentrations achieved in bulk by Boato *et al.*[1] by as much as two orders of magnitude in the case of Fe. As a result of the high concentrations covered in this study, it is possible to assert that, in agreement with Kaiser's theory,[2] the decrease of the critical temperature is exponential in the impurity concentration. An exponential decrease of T_c has been previously reported in an s-p–band superconductor[1] and in d- and f-band superconductors.[3–5] A further advantage of the present technique lies in the fact that the reference films are quite "dirty" (residual resistivity $\rho_0 \simeq 10^{-3}\ \Omega$ cm) and can be directly compared to Kaiser's theory for an isotropic superconductor without having to subtract, as in the case of bulk,[1,6] the anisotropy contribution as calculated by Markowitz and Kadanoff.[7] The fact that T_c is a well-behaved function of the impurity concentration supports the view that the enhancement in such films is homogeneous.[8,9] The excellent agreement between film-data and bulk-data points provides further support for recent susceptibility and NMR measurements[9] which suggest that many electronic properties of these aluminum films, amongst which the density of states is one, are very close to bulk values.

The experimental technique has been previously described.[8] The reference films were sputtered from a target made from an Al–10-wt%-Al_2O_3 powder mixture. The transition-metal elements were added as powders in the desired quantity to the Al-Al_2O_3 powder mixture. It is essential that all powders be smaller than 325 mesh in order to ensure a statistical distribution of impurities in the target. The composition of the targets as checked by x-ray-fluorescence analysis[10] was in all cases within ± 10% of the nominal composition. The composition of the films checked by the Coprex technique agreed with the composition of the sputtering target.[10] The films were deposited on sapphire substrates at 77 °K and were measured at liquid-helium temperatures without warming above 77 °K. The transition temperature was measured resistively and defined as the temperature where the smallest normal resistance can be detected.[11] The temperature width of all transitions (from 1 to 95% of the full normal resistance) was approximately 0.2 °K.

The transition temperature for Al–10-wt%-Al_2O_3 films as a function of the transition-metal concentration (Fe, Cr, and Mn) is shown in Fig. 1. The transition temperature (T_{co}) of the reference Al–10-wt%-Al_2O_3 film varies between 3 and 3.2 °K, but the T_c–vs–impurity-concentration curves seem to