near Fe^{+2} sites than near the Fe^{+3} sites. This stabilization lowers the electronic energy and increases the electronic excitation energy. This is to be contrasted with the Adler-Brooks mechanism[12] of the insulator-metal transition in which the transition is caused entirely by the splitting of the energy bands caused by the reduction of the lattice symmetry resulting from lattice distortion. Although this mechanism is present in the magnetite transition, the electronic interaction clearly plays a dominant role. If there is such a local polarization of the nonoctahedral-site ions, it could possibly be detected in a carefully done elastic-neutron-scattering experiment.

Recent elastic-neutron-diffraction experiments[19] have revealed peaks in addition to those predicted by the Verwey ordering. Recent Mössbauer data are consistent with these results.[20] Cullen and Callen have explained[10] these experiments by doing a three-dimensional energy-band calculation with four bands and three order parameters. The extra neutron peaks imply that not all sites are equivalent within a single row of Fe^{+3} or Fe^{+2} sites. This could conceivably also be caused by some sort of local lattice distortion, but the Cullen and Callen mechanism appears to be simpler. There still remains the question of why such ordering should occur, which is not answered by either explanation. We have not considered these effects in this paper. In order for the ordering of Ref. 10 to exist, the ions cannot be completely ordered as predicted by Verwey.[5,8] Further theoretical and experimental investigation is clearly needed to straighten out these points.

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Method of Executing the Tight-Binding Method of Energy-Band Calculation*

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This paper discusses a new technique for evaluating the matrix elements in tight-binding band calculations. The method employs an expansion of the crystal potential in reciprocal-lattice vectors and the atomic wave functions by a Fourier integral. The matrix elements are reduced to sums over the reciprocal lattice.

One of the difficulties associated with the tight-binding method of band-structure calculation is the evaluation of the matrix elements of the overlap matrix and Hamiltonian matrix. These matrix elements are weighted sums of many-center overlap and potential integrals. When the wave functions

involved extend over lattice sites, the sum converges very slowly, because the decrease in amplitude of the wave function is offset by an increase in the number of sites. This makes the series expression for the matrix elements converge slowly. Also, the numerical accuracy of many-centered integrals is poor when the separation between sites is large. Until recently, these difficulties have restricted the use of the tight-binding method; it is the purpose of this paper to describe a method to avoid the obstacles mentioned above.[1,2] Another method has been proposed[3] and used in actual calculations.[4,5] At the present time, no comparison has been carried out to determine the relative merits of the method discussed here and the other technique.

A tight-binding calculation begins with a choice of a set of atomic trial wave functions. The atomic trial wave functions are used to form trial Bloch functions in the manner shown below, and they are used to construct the crystal potential.[1,6] The trial Bloch functions, in the form for two atoms per unit cell of the lattice, are

$$\Psi_n(\vec{k},\vec{r})=\frac{1}{(N)^{1/2}}\sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j}\mu_n(\vec{r}-\vec{R}_j), \tag{1a}$$

$$\Psi_m(\vec{k},\vec{r})=\frac{1}{(N)^{1/2}}\sum_{\vec{R}_j} e^{i\vec{k}\cdot(\vec{R}_j+\vec{a})}\mu_m(\vec{r}-\vec{R}_j-\vec{a}), \tag{1b}$$

where $\vec{R}_j$ is the lattice-site vector and $\vec{a}$ is the vector displacement between the two types of atoms in the unit cell. The Hamiltonian, in terms of the crystal potentials V_A and V_B, is

$$H(\vec{r})=\tfrac{1}{2}\nabla^2+\sum_{\vec{R}_j}[V_A(\vec{r}-\vec{R}_j)+V_B(\vec{r}-\vec{R}_j-\vec{a})]. \tag{2}$$

The overlap matrix element is given by

$$\int_{-\infty}^{+\infty}\Psi_n^{\dagger}(\vec{k},\vec{r})\Psi_m(\vec{k},\vec{r})\,d\tau=S_{n,m}(\vec{k}) \tag{3}$$

and the Hamiltonian matrix element by

$$\int_{-\infty}^{+\infty}\Psi^{\dagger}(\vec{k},\vec{r})H(\vec{r})\Psi_m(\vec{k},\vec{r})\,d\tau=H_{n,m}(\vec{k}). \tag{4}$$

The difficulty of determining these matrix elements can be overcome by expanding the crystal potential in terms of reciprocal-lattice vectors and the trial atomic wave functions in terms of Fourier integrals.

Any function that possesses the periodicity of the lattice can be expanded in terms of the reciprocal-lattice vectors. A method of determing $V(\vec{r})$ is shown in Ref. 1. The crystal potential $V(\vec{r})$ meets the above requirement, so it can be expanded in terms of the reciprocal-lattice vectors. Thus we have

$$V(\vec{r})=\sum_{\vec{G}} e^{-\vec{G}\cdot\vec{r}}\,V(\vec{G}), \tag{5a}$$

where $\vec{G}$ is the reciprocal-lattice vector, $\vec{r}$ is the position vector in direct lattice, and

$$V(\vec{G})=(1/\Omega)\int_{\Omega} V(\vec{r})e^{i\vec{G}\cdot\vec{r}}\,d\tau, \tag{5b}$$

$$V(\vec{r})=\sum_{\vec{R}_j}[V_A(\vec{r}-\vec{R}_j)+V_B(\vec{r}-\vec{a}-\vec{R}_j)], \tag{6}$$

where Ω is the volume of the unit cell, $V_A(\vec{r})$ the potential of the A ion, and $V_B(\vec{r})$ the potential of the B ion. $\vec{a}$ is the position vector of site B with respect to site A. The reciprocal-lattice vectors $\vec{G}$ are determined using the primitive-basis vectors of the direct lattice. The $V(\vec{G})$ term can be calculated when the $\vec{G}$ has been determined:

$$V(\vec{G})=\frac{1}{\Omega}\int_{\Omega} e^{+\vec{G}\cdot\vec{r}}\sum_{\vec{R}_j}[V_A(\vec{r}-\vec{R}_j)+V_B(\vec{r}-\vec{a}-\vec{R}_j)]\,dr, \tag{7a}$$

$$V(\vec{G})=N[V_A(\vec{G})+e^{\vec{G}\cdot\vec{a}}V_B(\vec{G})], \tag{7b}$$

where N is the number of atoms of each type A or B within the crystal. In practice the integration over the primitive cell Ω is replaced by an integral over the Wigner-Seitz s sphere which is the sphere with the volume of the primitive cell. With the potential expressed in terms of the reciprocal-lattice vectors, we will now proceed to derive expressions for the overlap and Hamiltonian matrix elements.

To reexpress the overlap matrix element as a series dependent upon the reciprocal-lattice vectors, one begins with the tight-binding expression

$$(\Psi_m(\vec{r},\vec{k}),\Psi_m(\vec{r},\vec{k}))=\sum_{\vec{R}_j} e^{-i\vec{k}\cdot\vec{R}_j}\int_{-\infty}^{+\infty}\mu^*(\vec{r}-\vec{R}_j-\vec{a})\mu_m(\vec{r}-\vec{a})\,d\tau. \tag{8}$$

The wave function is next expressed as a Fourier integral

$$\mu_m(\vec{r}-\vec{R}_j-\vec{a})=\left(\frac{1}{2\pi}\right)^3\int_{-\infty}^{+\infty}U(\vec{q})\,e^{-i\vec{q}\cdot(\vec{r}-\vec{R}_j-\vec{a})}\,d\vec{q},$$
$$U(\vec{q})=\left(\frac{1}{2\pi}\right)^3\int_{-\infty}^{+\infty}e^{i\vec{q}\cdot\vec{r}'}\,\mu_m(\vec{r}')\,d\tau'. \tag{9}$$

It is instructive to determine the $U(\vec{q})$ for an "s"-type atomic wave function. The calculation of all the remaining angular momentum states proceeds in the same manner. The following identity is used in making the calculation:

$$e^{i\vec{q}\cdot\vec{r}}=\sum_{n=0}^{\infty}(2n+1)\,i^n P_n(\cos\theta)j_n(|\vec{q}|\,|\vec{r}|).$$

The integral over the radial coordinates can be

found in a table of integrals; the results of the integration over the angular coordinates are

$$U(\vec{q}) = \frac{(4\pi)^{1/2}}{|\vec{q}|} \int_0^\infty \sum_l C_l r^{n_l} e^{-\beta_l r} \sin(|\vec{q}| r)\, dr \ .$$

Now that $U(\vec{q})$ has been determined we can proceed with the derivation using the following relationships:

$$\int_{-\infty}^{+\infty} e^{-i(\vec{p}-\vec{q})2\pi\cdot\vec{r}}\, d\tau = (2\pi)^3 \delta(\vec{p}-\vec{q}), \tag{10}$$

$$\sum_{\vec{R}_j} e^{i\vec{R}_j\cdot(\vec{k}-\vec{p})} = [(2\pi)^3/\Omega] \sum_{\vec{\Delta}} \delta(\vec{k}+\vec{\Delta}, \vec{p}), \tag{11}$$

where $\vec{\Delta} \equiv$ reciprocal-lattice vector. Using Eqs. (9)–(11) in Eq. (8) results in the new expression for the overlap matrix element:

$$(\Psi_m(\vec{k},\vec{r}), \Psi_m(\vec{k},\vec{r})) = \frac{(2\pi)^3}{\Omega} \sum_{\vec{\Delta}} |U(\vec{k}+\vec{\Delta})|^2. \tag{12}$$

The reexpression of Hamiltonian matrix elements in terms of the reciprocal-lattice vectors proceeds in the same way as the overlap matrix element. In this case, the matrix element is equal to the sum of two parts; one part is the kinetic-energy matrix element, the second is the crystal-potential matrix element. The kinetic-energy matrix element is given by

$$(\Psi_m(\vec{k},\vec{r}), \tfrac{1}{2}\nabla^2\Psi_m(\vec{k},\vec{r})) = -\frac{1}{2}\ \frac{(2\pi)^3}{\Omega} \sum_{\vec{\Delta}} [(\vec{k}+\vec{\Delta})\cdot(\vec{k}+\vec{\Delta})]\, |U(\vec{k}+\vec{\Delta})|^2, \tag{13}$$

and the potential-energy matrix element by

$$(\Psi_m(\vec{k},\vec{r}), \{\sum_{\vec{R}_j} [V_A(\vec{r}-\vec{R}_j) + V_B(\vec{r}-\vec{R}_j-\vec{a})]\} \Psi_m(\vec{k},\vec{r})) = \frac{(2\pi)^3}{\Omega} \sum_{\vec{\Delta}} \sum_{\vec{G}} V(\vec{G}) e^{-i\vec{a}\cdot\vec{G}} U^*(\vec{G}+\vec{k}+\vec{\Delta}) U(\vec{k}+\vec{\Delta}). \tag{14a}$$

The exponential $e^{-i\vec{a}\cdot\vec{G}}$ in the series represents the effect of the origin of the A sites being translated from the B sites by the vector $\vec{a}$. Replacing $V(\vec{G})$ in Eq. (14a) by Eq. (7b) gives

$$(\Psi_m(\vec{k},\vec{r}), V(\vec{r})\Psi_m(\vec{k},\vec{r})) = \frac{(2\pi)^3}{\Omega} \sum_{\vec{\Delta}} \sum_{\vec{G}} [V_A(\vec{G}) e^{-i\vec{G}\cdot\vec{a}} + V_B(\vec{G})] \times U^*(\vec{G}+\vec{k}+\vec{\Delta}) U(\vec{k}+\vec{\Delta}). \tag{14b}$$

The success of the above method depends upon rapid convergence of the double summations in (14a) and (14b).

The actual convergence of particular series summations over $\vec{G}$ cannot be determined in advance, since convergence depends upon $\mu(\vec{r})$, $V(\vec{r})$, crystal symmetry, and the size of the primitive cell. Also, convergence is controlled by the value of $\vec{k}$ and whether or not it is a symmetry point of the Brillouin zone. The series for the overlap and kinetic energy converge rapidly compared with the series for the potential. The convergence problem results from the oscillation in $U(\vec{G})$ for large values of $\vec{G}$, and the large number of vectors associated with a large $|\vec{G}|$. This problem of convergence is essential to the question of whether or not this method is practical, and each user must decide for himself at the present time. Later sum rules may be developed.

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