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Energy band with Wannier functions of ferromagnetic symmetry as the cause of ferromagnetism in iron

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It is shown that iron possesses an energy band with Bloch functions which can be unitarily transformed into optimally localized Wannier functions belonging to a corepresentation of the magnetic group $M = I4/mm'm'$ of ferromagnetic iron. As compared to the other bands of iron, this ''ferromagnetic band'' is extremely narrow. In paramagnetic iron, it is roughly half-filled, and in ferromagnetic iron, it is nearly empty for the minority-spin states and nearly filled for the majority-spin states. These findings can be interpreted within the group-theoretical nonadiabatic Heisenberg model as proposed by the author for better understanding of superconductivity and spin-density-wave states. In the framework of this model, the localized states in the Heisenberg model are no longer represented by atomic or Wannier functions but by more realistic nonadiabatic localized functions which have the same symmetry as the Wannier functions. The related nonadiabatic Hamiltonian H^n has the correct symmetry of the ferromagnetic state because it does not commute with the operator K of time inversion. From the symmetry of H^n it follows that the ground state $|G^n\rangle$ of H^n possesses a spin structure with the magnetic group M. Furthermore, it is argued that an operator commuting with K only has nonmagnetic *eigenstates*. Hence, there is evidence that the ferromagnetic band causes the stability of the ferromagnetic state in iron. [S0163-1829(99)05021-3]

I. INTRODUCTION

In his original theory of magnetism, Heisenberg[1] extended the well-known Heitler-London model of the hydrogen molecule to the metals by assuming that there is exactly one electron at each atom of a metal. This assumption, which is often referred to as the Heisenberg model, leads to a fundamental understanding of magnetism, although in most metals electrons belonging to partly filled energy bands are responsible for magnetism. In such bands the electrons may hop from one atom to another when performing their band motion. There is strong theoretical and experimental evidence that, e.g., the d electrons of the transition metals exhibit behavior of both the band and the Heisenberg model.[2]

The nonadiabatic Heisenberg model as proposed in this and previous papers[3–5] generalizes the original Heisenberg model by introducing three new postulates which will be given in the following Sec. II. The essential physical statement of this model is expressed by the second postulate given in Eq. (2.13). It replaces the strong original assumption of the Heisenberg model by stating that the balance between bandlike and atomiclike behavior is shifted *as far as possible* towards the atomiclike behavior in narrow energy bands.

The second postulate of the nonadiabatic Heisenberg model cannot be satisfied within the adiabatic (or Born-Oppenheimer) approximation, which represents the localized states by Wannier functions. These functions describe localized electrons which move in *rigid* orbitals in the average potential of the other electrons. The second postulate, however, requires a more realistic description of the electronic motion within the localized states. In the true (nonadiabatic) system a localized electron moves in a potential depending on which of the adjacent localized states is occupied and on the present motion of the electrons in these states. Within the nonadiabatic Heisenberg model, these modified orbitals are described by introducing a new quantum number ν which labels different states of motion of the center of mass of the localized states.

The essential properties of the nonadiabatic localized states are fixed by the three postulates of the nonadiabatic Heisenberg model. As a consequence, the nonadiabatic localized functions (representing the nonadiabatic localized states) have the same symmetry as the Wannier functions of the narrowest, roughly half-filled energy bands of the metal under consideration. Thus, any application of the nonadiabatic Heisenberg model starts with a group-theoretical examination of the symmetry of the best localized Wannier functions which is determined by the symmetry of the Bloch functions in the band structure of the given metal.[6–8]

However, the partly filled bands in the (paramagnetic) band structures of the metals are degenerate at some symmetry points and lines of the Brillouin zone. Therefore, it is not possible to separate narrow single bands (or narrow isolated sets of bands) which satisfy the compatibility relations throughout the Brillouin zone. Thus, the Bloch functions of the narrowest, roughly half-filled energy bands cannot be unitarily transformed into Wannier functions which are *both* symmetry adapted to the paramagnetic space group M^P of the considered metal *and* best localized.[6,7] Therefore, the exact Wannier functions are often replaced by approximated Wannier functions ignoring the band degeneracies. These approximated Wannier functions are constructed from the Bloch functions by a transformation which is nearly but not exactly unitary. Such Wannier functions, however, *are not allowed* within the nonadiabatic Heisenberg model.

An (exactly) unitary transformation of the Bloch functions of the conduction bands into best localized Wannier functions becomes possible in a lot of metals when the Wannier functions are allowed to have a reduced symmetry or

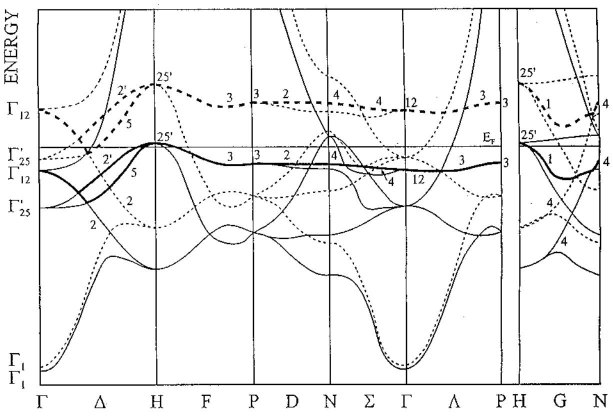

FIG. 1. Band structure of ferromagnetic iron after Callaway and Wang (Ref. 16). Solid lines are majority-spin states; dashed are minority-spin states. The heavy lines denote the ferromagnetic (FM) band which has the symmetry of band 2 in Table I.

when they are allowed to be spin dependent.[8] There are two interesting cases.

(1) The Wannier functions are symmetry adapted to the complete paramagnetic group M^P but are spin dependent.

(2) The Wannier functions still are spin *in*dependent but are symmetry adapted only to a magnetic subgroup M of M^P.

In the first case, an absolutely new exchange mechanism can be established within the nonadiabatic Heisenberg model. This mechanism is proposed to be the cause of superconductivity.[3,5] The second case is considered in this paper.

Paramagnetic iron possesses an energy band with Bloch functions which can be unitarily transformed into optimally localized Wannier functions belonging to a one-dimensional corepresentation of the magnetic group $M = I4/mm'm'$ of the ferromagnetic state; see Appendix A. Furthermore, it is not possible to choose these Wannier functions to be real. As compared to the other bands of iron, this ''ferromagnetic (FM) band'' is extremely narrow. In paramagnetic iron, it is roughly half-filled. In ferromagnetic iron, on the other hand, it is nearly empty for the minority-spin states and nearly filled for the majority-spin states; see Fig. 1.

Within the nonadiabatic Heisenberg model, the FM band causes the stability of the ferromagnetic state in iron. In Sec. III A it shall be shown that the postulates of the nonadiabatic Heisenberg model force a ferromagnetic spin structure in the FM band. That means, *if* the postulates are satified within an FM band, *then* the electron spins form a spin structure possessing the magnetic group *M*.

The result of Sec. III A is confirmed in the following Sec. III B. Here, from the properties of the nonadiabatic localized functions alone, it shall be deduced that the nonadiabatic Hamiltonian H^n of the FM band is spin dependent and that the ground state $|G^n\rangle$ of H^n possesses a spin structure with the magnetic group M of ferromagnetic iron.

In Appendix A, the symmetry of the Wannier functions of the FM band will be given. In the following Appendix B, the essential properties of the related nonadiabatic localized functions will be deduced from the postulates of the nonadiabatic Heisenberg model. Since further properties of these functions are unknown, they only serve to derive general properties of H^n.

II. NONADIABATIC HEISENBERG MODEL

Consider a single partly filled energy band in a metal with one atom in the unit cell. For the present considerations, this band need not be an FM band. Let

$$H = H_{HF} + H_{Cb} \tag{2.1}$$

be the electronic Hamiltonian of this band with H_{HF} and

$$H_{Cb} = \sum_{\vec{T},s} \langle \vec{T}_1, \vec{T}_2 | H_{Cb} | \vec{T}'_1, \vec{T}'_2 \rangle c^{\dagger}_{\vec{T}_1 s_1} c^{\dagger}_{\vec{T}_2 s_2} c_{\vec{T}'_2 s_2} c_{\vec{T}'_1 s_1}, \tag{2.2}$$

representing the Hartree-Fock and Coulomb energy, respectively. The fermion operators $c^{\dagger}_{\vec{T}s}$ and $c_{\vec{T}s}$ create and annihilate electrons with spin s in the localized states $|\vec{T}\rangle$ represented by Wannier functions $w(\vec{r} - \vec{T})$. They are assumed to be situated at the atoms and to form a complete basis within the considered band. Other contributions to H from the electrons not belonging to this band are neglected even as are spin-orbit effects.

H_{Cb} may be written as

$$H_{Cb} = H_c + H_{ex} + H_z, \tag{2.3}$$

with the operator of Coulomb repulsion, H_c, containing all the matrix elements of H_{Cb} with

$$\vec{T}_1 = \vec{T}'_1 \text{ and } \vec{T}_2 = \vec{T}'_2, \tag{2.4}$$

the exchange operator H_{ex} containing the matrix elements with

$$\vec{T}_1 = \vec{T}'_2 \text{ and } \vec{T}_2 = \vec{T}'_1, \tag{2.5}$$

and H_z comprising the remaining matrix elements, i.e., the matrix elements with

$$\{\vec{T}_1, \vec{T}_2\} \neq \{\vec{T}'_1, \vec{T}'_2\}. \tag{2.6}$$

The matrix elements of H_z satisfy neither Eq. (2.4) nor (2.5). Thus, H_z represents an interaction annihilating two electrons in the localized states at the positions $\vec{T}'_1$ and $\vec{T}'_2$ and creating at least one of them at the new positions $\vec{T}_1$ or $\vec{T}_2$. Hence, unlike H_c or H_{ex}, the operator H_z generates virtual transitions between adjacent localized states which shift the balance between the bandlike and atomiclike behavior of the electrons toward the bandlike character. Let

$$H' = H_{HF} + H_c + H_{ex} \tag{2.7}$$

be the Hamiltonian obtained from H by putting $H_z = 0$. Assume the considered band to be sufficiently narrow that the ground state $|G'\rangle$ of H' clearly has atomiclike character. This atomiclike character will be less pronounced in the ground state $|G\rangle$ of the complete Hamiltonian H because of the influence of the interaction H_z. Thus, the probability to find two electrons (with different spin directions) on the same lattice point $\vec{T}$ will be larger in $|G\rangle$ than in $|G'\rangle$. Therefore, the total Coulomb repulsion energy in the state $|G\rangle$ should be greater than in the state $|G'\rangle$ because the Coulomb repulsion of two electrons occupying localized states on the same lattice point $\vec{T}$ is larger than the Coulomb repulsion of two electrons occupying adjacent localized states.[9]

Hence, we may assume that in sufficiently narrow, partly filled energy bands we have

$$\langle G|H|G\rangle > \langle G'|H'|G'\rangle, \tag{2.8}$$

where $|G\rangle$ and $|G'\rangle$ are the *exact* ground states of H [given in Eq. (2.1)] and H', respectively. The first postulate of the nonadiabatic Heisenberg model states that relation (2.8) is satisfied for the narrowest, roughly half-filled bands of the metals.[3]

The particular form of the matrix elements of H_z shows that it represents a short-ranged interaction which crucially depends on the exact form of the localized functions. This fact suggests that only small changes of the localized electronic orbitals are required to prevent (at least partially) the transitions generated by H_z. Such modifications of the electronic orbitals do not exist within the adiabatic approximation because these modifications yield charge distributions within the localized states, being symmetric with respect to the lattice on the average of time, but not at any moment. Consequently, the nuclei become permanently accelerated in varying directions. Therefore, we replace the (adiabatic) localized states represented by the Wannier functions by more realistic nonadiabatic localized states,

$$|\vec{T},m,\nu\rangle, \tag{2.9}$$

which take into account the motion of the nuclei. The new quantum number ν labels different states of motion of the center of mass of the nucleus and the electron occupying the state $|\vec{T},m,\nu\rangle$. (With free atoms, the nonadiabatic motion of the nuclei occurs in such a way that the total center of mass stays at rest. In a solid state, consisting of bound atoms, this restriction does not hold.) The quantum number m of the crystal spin[3] replaces the spin quantum number s in the nonadiabatic system.

The nonadiabatic Hamiltonian H^n may be written as

$$H^n = H_{HF} + H^n_{Cb}, \tag{2.10}$$

where the Coulomb interaction now has the form

$$\begin{aligned} H^n_{Cb} = \sum_{\vec{T},m} & \langle \vec{T}_1,m_1,n;\vec{T}_2,m_2,n|H_{Cb}|\vec{T}'_1,m'_1,n;\vec{T}'_2,m'_2,n\rangle \\ & \times c^{n\dagger}_{\vec{T}_1m_1} c^{n\dagger}_{\vec{T}_2m_2} c^{n}_{\vec{T}'_2m'_2} c^{n}_{\vec{T}'_1m'_1}. \end{aligned} \tag{2.11}$$

The new fermion operators $c^{n\dagger}_{\vec{T}m}$ and $c^{n}_{\vec{T}m}$ create and annihilate electrons with crystal spin m in the nonadiabatic localized states $|\vec{T},m,n\rangle$. The matrix elements of H^n_{Cb} are integrals over nonadiabatic localized functions

$$\langle \vec{r},t,\vec{q}\ \ |\vec{T},m,n\rangle, \tag{2.12}$$

as given in Eq. (2.13) of Ref. 4, and $\nu = n$ labels the nonadiabatic states which satisfy the following Eqs. (2.13) and (4.2). The new coordinate $\vec{q}$ represents that part of the motion of the nuclei which nonadiabatically follows the motion of the electron occupying the state $|\vec{T},m,n\rangle$ and t is the spin coordinate; see Appendix B.

The electronic orbital in a state $|\vec{T},m,\nu\rangle$ depends very much on ν since the mass of the electron is considerably smaller than the mass of the nucleus. In the nonadiabatic system, the electrons no longer move in *rigid* orbitals in the average potential of the other electrons, but move in a potential depending on which of the adjacent localized states are occupied and on the present positions of these electrons. Hence, the electrons should be able to avoid the transitions generated by H_z by an appropriately modified motion, if these transitions are energetically unfavourable, i.e., if relation (2.8) is true. Thus, as a consequence of relation (2.8), all the matrix elements of H^n_{Cb} which satisfy neither Eq. (2.4) nor Eq. (2.5) should vanish.

For this reason, we assume that there exist nonadiabatic localized functions satisfying

$$\langle \vec{T}_1,m_1,n;\vec{T}_2,m_2,n|H_{Cb}|\vec{T}'_1,m'_1,n;\vec{T}'_2,m'_2,n\rangle = 0 \tag{2.13}$$

if

$$\{\vec{T}_1,\vec{T}_2\} \neq \{\vec{T}'_1,\vec{T}'_2\}.$$

This Eq. (2.13) is the second postulate of the nonadiabatic Heisenberg model.

As a consequence of Eq. (2.13), the commutation properties of the operator H^n_{Cb} depend on the symmetry properties of the nonadiabatic localized states. Since only small modifications of the adiabatic electronic orbitals are required to prevent the transitions generated by H_z, we may assume that the nonadiabatic Hamiltonian H^n has the same commutation properties as the adiabatic Hamiltonian H' given in Eq. (2.7), i.e.,

$$[H',P]\left\{\begin{matrix} = \\ \neq \end{matrix}\right\}0 \ \Rightarrow\ [H^n,P]\left\{\begin{matrix} = \\ \neq \end{matrix}\right\}0, \tag{2.14}$$

where P stands for any symmetry operator.

According to its definition, the operator H' arises from the complete adiabatic Hamiltonian H in Eq. (2.1) by putting

$$H_z = 0. \tag{2.15}$$

This equation does not state that H_z is *neglected*, but that H_z is *put equal to zero*. By this step, the commutation properties of H' depend on the symmetry of the Wannier functions $w(\vec{r}-\vec{T})$ (whereas the commutation properties of the complete Hamiltonian H are independent of the symmetry of the used basis functions). As a consequence of relation (2.14), the nonadiabatic localized functions have the same symmetry as the Wannier functions $w(\vec{r}-\vec{T})$. Equation (2.14) is the third (and last) postulate of the nonadiabatic Heisenberg model.

It is not possible to calculate any matrix elements of H^n_{Cb} since the nonadiabatic functions $\langle \vec{r},t,\vec{q}\ \ |\vec{T},m,n\rangle$ are unknown apart from the properties given in Appendix B. The nonadiabatic Heisenberg model is a purely group-theoretical model which analyses the symmetry and spin dependence of H^n.

The operator H^n_{Cb} given in Eq. (2.11) has nonvanishing matrix elements with

$$\{m_1,m_2\}\neq\{m'_1,m'_2\},$$

violating the conservation of crystal spin. These matrix elements are the cause of an interaction between the electron spins and the phonons.[3] In this paper, this spin-phonon interaction is ignored.

III. APPLICATION OF THE NONADIABATIC HEISENBERG MODEL TO FERROMAGNETIC IRON

A. Ferromagnetic spin structure in the nonadiabatic ground state

Now assume that the energy band considered in the previous Sec. II to be the FM band of iron denoted in Fig. 1 by the heavy lines. It is extremely narrow and roughly half-filled in paramagnetic iron. Hence, we have optimal conditions[3] for a relatively great value of

$$\Delta E=\langle G|H|G\rangle-\langle G'|H'|G'\rangle. \tag{3.1}$$

We first examine the commutation properties of the operator H' given in Eq. (2.7). The matrix elements of H' satisfy Eq. (2.4) or (2.5), since H_z is put equal to zero. As a consequence of Eqs. (A25) and (A26) it follows that H' commutes with the symmetry operators $P(a)$ and $KP(a)$ of the magnetic group $M=G+K\{C_{2x}|\vec{0}\}G$ [see Eq. (A2)] of ferromagnetic iron,

$$[H',P(a)]=0 \quad \text{for} \quad a\in G \tag{3.2}$$

and

$$[H',KP(a)]=0 \quad \text{for} \quad a\in\{C_{2x}|\vec{0}\}G, \tag{3.3}$$

because also the matrix elements of the operators $P(a)H'P^{-1}(a)$ (with $a\in G$) and $KP(a)H'P^{-1}(a)K^{-1}$ (with $a\in\{C_{2x}|\vec{0}\}G$) satisfy Eq. (2.4) or (2.5).

Equations (A20), (A23), and (A24), on the other hand, show that $KH'K^{-1}$ has matrix elements violating Eqs. (2.4) and (2.5). Therefore, H' does not commute with the operator K of time inversion,

$$[H',K]\neq 0. \tag{3.4}$$

According to the third postulate (2.14) of the nonadiabatic Heisenberg model, the nonadiabatic operator H^n also commutes with the operators $P(a)$ and $KP(a)$ of the group M,

$$[H^n,P(a)]=0 \quad \text{for} \quad a\in G \tag{3.5}$$

and

$$[H^n,KP(a)]=0 \quad \text{for} \quad a\in\{C_{2x}|\vec{0}\}G, \tag{3.6}$$

and *does not commute* with the operator K of time inversion,

$$[H^n,K]\neq 0. \tag{3.7}$$

Thus, H^n commutes *only* with the symmetry operators of M, while the complete adiabatic Hamiltion H in Eq. (2.1) commutes with all the operators $P(a)$ of the space group O_h^9 of bcc paramagnetic iron,

$$[H,P(a)]=0 \quad \text{for} \quad a\in O_h^9, \tag{3.8}$$

and with the operator K of time inversion,

$$[H,K]=0. \tag{3.9}$$

The operator H^n does not possess the bcc symmetry of the paramagnetic lattice. From Eqs. (3.5), (3.6), and (3.7) it follows that the ground state $|G^n\rangle$ of H^n satisfies the equations

$$P(a)|G^n\rangle=|G^n\rangle \quad \text{for} \quad a\in G, \tag{3.10}$$

$$KP(a)|G^n\rangle=|G^n\rangle \quad \text{for} \quad a\in\{C_{2x}|\vec{0}\}G, \tag{3.11}$$

and

$$K|G^n\rangle\neq|G^n\rangle. \tag{3.12}$$

These equations show that in $|G^n\rangle$ the electrons move *as if* there exists a potential with the magnetic group M, which means that they move as if there exists a ferromagnetic spin structure. Such a motion is possible if *and only if* a spin structure with the magnetic group M exists in reality. Hence, the second postulate (2.13) of the nonadiabatic Heisenberg model may be satisfied only if there exists a ferromagnetic spin structure with the magnetic group M. In the following Sec. III B it will be shown that, actually, H^n is spin dependent in the FM band.

B. Magnetic state as eigenstate of a real Hamiltonian

The important Equation (3.7) could not be understood in the framework of the adiabatic approximation since the original operator of Coulomb interaction,

$$\tilde{H}_{Cb}=\frac{1}{2}\sum_{\substack{\mu,\nu\\ \mu\neq\nu}}\frac{e^2}{|\vec{r}_\mu-\vec{r}_\nu|}, \tag{3.13}$$

is real and, hence, commutes with the operator K of time inversion,

$$[\tilde{H}_{Cb},K]=0. \tag{3.14}$$

Therefore, within the adiabatic approximation it is not possible in any way to turn this operator into an operator not commuting with K.

The nonadiabatic operator of Coulomb interaction in the FM band [as given in Eq. (2.11)] may be written as

$$H^n_{Cb}=F_{\mathcal{A}}\tilde{H}_{Cb}F_{\mathcal{A}}, \tag{3.15}$$

where the projection operator

$$F_{\mathcal{A}}=\sum_{\vec{T},m}c^{n\dagger}_{\vec{T}m}c^{n}_{\vec{T}m} \tag{3.16}$$

projects on the space $\mathcal{A}$ of wave functions which satisfy the Pauli principle within the FM band. From Eqs. (3.7) and (3.14) it follows that it is the projection operator $F_{\mathcal{A}}$ which does not commute with K,

$$[F_{\mathcal{A}},K]\neq 0. \tag{3.17}$$

This equation is true if

$$Kc^{n\dagger}_{\vec{T}m}K^{-1}\notin \mathcal{A}. \tag{3.18}$$

As shown in Appendix B, Eq. (3.18) is satisfied if (and only if) the quantum numbers n_1 and n_2 in Eq. (B8) are different. That means that, if $n_1\neq n_2$, the nonadiabatic operator H^n_{Cb} does not commute with K, *although the operator* $\tilde{H}_{Cb}$ *is real* and, hence, Eq. (3.7) does not violate physical principles.

Since the quantum numbers n_1 and n_2 are different, the nonadiabatic localized functions cannot be written as a product of a function depending on $\vec{r}$ and $\vec{q}$ and Pauli's spin function [see Eq. (B2)],

$$\langle\vec{r},t,\vec{q}|\vec{T},m,n\rangle\neq\langle\vec{r},\vec{q}|\vec{T},n\rangle u_s(t). \tag{3.19}$$

This equation demonstrates that, as a consequence of the postulates of the nonadiabatic Heisenberg model, the nonadiabatic operator H^n_{Cb} of Coulomb interaction has become spin dependent. H^n_{Cb} no longer commutes with the symmetry operators $S(\alpha)$ of the electron spin [see Eq. (B3)],

$$[H^n_{Cb},S(\alpha)]=0 \quad \textit{only} \;\text{ for }\; \alpha=E \tag{3.20}$$

and, hence,

$$S(\alpha)|G^n\rangle=|G^n\rangle \quad \textit{only} \;\text{ for }\; \alpha=E, \tag{3.21}$$

where E denotes the identity operation. This equation confirms the statement of the preceding Sec. III A that the nonadiabatic ground state $|G^n\rangle$ possesses a spin structure. According to Eqs. (3.5) and (3.6) this spin structure has the magnetic group M of ferromagnetic iron.

IV. EXCHANGE ENERGY

The considerations in the preceding Sec. III may be summarized by an if-then statement: *if* the postulates of the nonadiabatic Heisenberg model are satisfied within the FM band, *then* the electrons of this band move in orbitals which are adapted to the symmetry of the magnetic group M. That means that they move *as if* there exists a ferromagnetic spin structure with the group M. From this we concluded that such a spin structure really exists. This conclusion, however, contains the tacit assumption that an electron of the FM band ''sees'' the spin directions of the other electrons. Thus, we must assume that any localized electron of the FM band moves in a spin-dependent potential generated by the other electrons and that this movement occurs in such a manner that the potential energy related to this spin-dependent potential is minimum. In this case, the electrons of the FM band *really* move in orbitals which are adapted to the symmetry of the magnetic group M.

The required spin-dependent potential exists: it is generated by exchange interaction. The mentioned ''potential energy related to this spin-dependent potential'' is the exchange energy. The energy $E^n=\langle G^n|H^n|G^n\rangle$ of the nonadiabatic ground state may be written as

$$E^n=E-E_{ex}, \tag{4.1}$$

where E_{ex} stands for the total exchange energy of the electrons of the FM band within the spin-dependent potential of all the electrons at the Fermi level (and E denotes the remaining energy). If the postulates of the nonadiabatic Heisenberg model are satisfied within the FM band, then the electrons occupying the nonadiabatic localized states move in such a way that the exchange energy E_{ex} is maximum,

$$E_{ex}=\text{maximum}, \tag{4.2}$$

for a spin structure with the magnetic group M. In this case, the electrons of the FM band move in orbitals which are adapted to the symmetry of M.

Consider the interatomic exchange interaction in the FM band. As is well known, from H_{ex} [given in Eq. (2.3)] the familiar Heisenberg exchange operator

$$H_s=-\frac{1}{\hbar^2}\sum_{\vec{T}_1\neq\vec{T}_2}\langle\vec{T}_1,\vec{T}_2|H_{Cb}|\vec{T}_2,\vec{T}_1\rangle\vec{S}_{\vec{T}_1}\vec{S}_{\vec{T}_2} \tag{4.3}$$

may be derived under the assumption that there is one electron at each atom. (The operators $\vec{S}_{\vec{T}}$ denote spin operators at position $\vec{T}$.) Also in the nonadiabatic system we may assume the operator

$$H^n_{ex}=\sum_{\vec{T},m}\langle\vec{T}_1,m_1,n;\vec{T}_2,m_2,n|H_{Cb}|\vec{T}_2,m'_1,n;\vec{T}_1,m'_2,n\rangle \times c^{n\dagger}_{\vec{T}_1m_1}c^{n\dagger}_{\vec{T}_2m_2}c^{n}_{\vec{T}_1m'_2}c^{n}_{\vec{T}_2m'_1} \tag{4.4}$$

to produce the required spin-dependent potential within the FM band.

As already mentioned, in the nonadiabatic localized states $|\vec{T},m,\nu\rangle$ the electrons no longer move in rigid orbitals in the average potential of the other electrons, but move in a potential depending on which of the adjacent localized states are occupied and on the present positions of these electrons. This modified motion is labeled by the new quantum number ν. The matrix elements of both the Hartree-Fock operator H_{HF} and the operator of Coulomb repulsion energy, H^n_c [see Eq. (2.3)], will not markedly depend on ν since they only depend on the charge distributions $|\langle\vec{r},t,\vec{q}\;\;|\vec{T},m,\nu\rangle|^2$ in the localized states. The matrix elements of H^n_{ex}, on the other hand, have the same form as the matrix elements of H^n_z and, hence, depend sensitively on the exact form of the localized functions. Thus, the exchange energy

$$E^{FM}_{ex}=-\langle G^n|H^n_{ex}|G^n\rangle \tag{4.5}$$

will also depend sensitively on the exact form of the electronic orbitals within the nonadiabatic localized states. If the postulates of the nonadiabatic Heisenberg model are satisfied within the FM band, the electrons modify their orbitals within the nonadiabatic localized states in such a way that the exchange energy E^{FM}_{ex} is maximum for a ferromagnetic spin structure.

Though the simple exchange operator H_s in Eq. (4.3) may be derived from H^n_{Cb} only under the strong [cf. Eq. (3.19)] approximation

$$\langle \vec{T}_1,m_1,n;\vec{T}_2,m_2,n|H_{Cb}|\vec{T}_2,m'_1,n;\vec{T}_1,m'_2,n\rangle$$
$$\approx\langle \vec{T}_1,n;\vec{T}_2,n|H_{Cb}|\vec{T}_2,n;\vec{T}_1,n\rangle \delta_{m'_1m_1}\delta_{m'_2m_2}, \quad (4.6)$$

we may assume that also in the nonadiabatic system the exchange energy E^{FM}_{ex} is maximum if there is exactly one electron at each atom. Hence, there are optimal conditions for a large exchange energy E^{FM}_{ex} in iron since Eq. (2.13) produces a ground state in which a maximum number of atoms is occupied by only one electron of the FM band.

The condensation energy E_f, i.e., the energy difference between the paramagnetic and the ferromagnetic state, is given by

$$E_f=\Delta E+E_{ex}, \quad (4.7)$$

where ΔE is given in Eq. (3.1). E_f may be positive even if E_{ex} is negative.

V. TIME-INVERSION SYMMETRY

The operator K of time inversion reverses the direction of a magnetic moment. Thus, the application of K on any magnetic state $|m\rangle$ yields a state differing from $|m\rangle$,

$$K|m\rangle\neq|m\rangle, \quad (5.1)$$

since K transforms the spin structure of $|m\rangle$ into the reversed structure.

The nonadiabatic Hamiltonian H^n derived in this paper does not commute with K,

$$[H^n,K]\neq 0. \quad (5.2)$$

Hence, H^n has the correct magnetic symmetry, since its ground state $|G^n\rangle$ is not an eigenstate of K,

$$K|G^n\rangle\neq|G^n\rangle. \quad (5.3)$$

Thus, from Eq. (5.2) alone it follows that $|G^n\rangle$ is magnetic.

On the other hand, there is evidence that all the *eigenstates* of the adiabatic Hamiltonian H given in Eq. (2.1) do not possess a magnetic structure because H commutes with K. Therefore, the eigenstates of H may be chosen such that they are eigenstates of K, too. If the number N of electrons is even, all the eigenstates $|e_i\rangle$ of K may be chosen in such a way[10] that they satisfy

$$K|e_i\rangle=|e_i\rangle; \quad (5.4)$$

i.e., they are not magnetic.

If N is odd, the (anti-unitary) operator K does not possess eigenstates and we cannot exclude in this way that H has magnetic eigenstates. However, a magnetic structure in a state consisting of many electrons should be stable for both odd and even numbers N of electrons. Hence, we may suppose that in any metal the complete adiabatic Hamiltonian H does not possess *eigenstates* in which the spins form a magnetic structure.

TABLE I. Single-valued representations $R_{\vec{k}}$ of the eight possible ferromagnetic bands in bcc metals in the C^5_{4h} notation of Table III. Bands 3, 4, 7, and 8 form ferromagnetic bands in any band structure since the Wannier functions related to these bands cannot be chosen to be real. It can be examined by Table II whether or not also bands 1, 2, 5, and 6 form ferromagnetic bands in a given band structure.

1	Γ_1^+	P_1	X_1^+	Z_1^+	N^+
2	Γ_2^+	P_2	X_1^+	Z_2^+	N^+
3	Γ_3^+	P_3	X_2^+	Z_3^+	N^+
4	Γ_4^+	P_4	X_2^+	Z_4^+	N^+
5	Γ_1^-	P_2	X_1^-	Z_1^-	N^-
6	Γ_2^-	P_1	X_1^-	Z_2^-	N^-
7	Γ_3^-	P_4	X_2^-	Z_3^-	N^-
8	Γ_4^-	P_3	X_2^-	Z_4^-	N^-

VI. CHOICE OF THE FERROMAGNETIC BAND IN THE BAND STRUCTURE OF IRON

An energy band in a bcc metal is called a FM band if, first, the Bloch functions of this band can be unitarily transformed into Wannier functions which are best localized, symmetry adapted to the magnetic group $M=I4/mm'm'$ of the ferromagnetic state, and situated at the atoms, and if, second, these Wannier functions cannot be chosen to be real. In bcc metals, FM bands may be identified by means of the Tables I, II, and III; see Appendix A. Within the nonadiabatic Heisenberg model, the FM band should be one of the narrowest (roughly) half-filled bands in the band structure of the paramagnetic metal.

Consider the band structure of iron as given in Fig. 1. The narrowest, partly filled band is characterized by H'_{25} and P_3. Table III shows that the three fold-degenerate state with H'_{25} symmetry splits into three states with Z_2^+, Z_3^+, and Z_4^+ symmetry at the transition from the paramagnetic space group O^9_h to the ferromagnetic space group C^5_{4h}. In the same way, P_3 splits into P_1 and P_2.

TABLE II. Single-valued representations $R_{\vec{k}}$ of eight bands in the D^{17}_{4h} notation of Table III. Each band is related to the band of Table I given in the first column. Assume that in a given band structure a band of the symmetry type of band j $(j=1,2,5,6)$ of Table I is present. Assume further the symmetry of this band to be written in the D^{17}_{4h} notation of Table III, too. Band j does not form a ferromagnetic band if the D^{17}_{4h} notation of this band can be found among the two bands related to band j in this Table II, because, in this case, the Wannier functions may be chosen to be real.

1	Γ_1^+	P_1	X_1^+	Z_1^+	N_1^+
	Γ_2^+	P_2	X_3^+	Z_2^+	N_2^+
2	Γ_3^+	P_3	X_3^+	Z_3^+	N_1^+
	Γ_4^+	P_4	X_1^+	Z_4^+	N_2^+
5	Γ_1^-	P_3	X_1^-	Z_1^-	N_1^-
	Γ_2^-	P_4	X_3^-	Z_2^-	N_2^-
6	Γ_3^-	P_1	X_3^-	Z_3^-	N_1^-
	Γ_4^-	P_2	X_1^-	Z_4^-	N_2^-

TABLE III. Compatibility relations between O_h^9, the space group of bcc paramagnetic iron, and the space groups C_{4h}^5 and D_{4h}^{17}. The space group C_{4h}^5 of the ferromagnetic state has the point group C_{4h}, and the related ''magnetic overgroup'' D_{4h}^{17} with the point group D_{4h} is given by Eq. (A8). The first row lists the irreducible representations at the symmetry points in the Brillouin zone Γ_c^v of O_h^9 in the notation of Bouckaert, Smoluchowski, and Wigner (Ref. 13) as given in Appendix 3-3 of Ref. 14. The following rows list representations at the corresponding points in the Brillouin zone Γ_q^v of C_{4h}^5 and D_{4h}^{17} in the notation of Koster *et al* (Ref. 15) as given in Table 2.2 of Ref. 10. The representations in the same column are compatible in the sense that a set of basis functions of the representation in the first row forms also a basis of the representations below. It should be noted that the representations in Γ_c^v and Γ_q^v are different even if they have the same name. (a) Points Γ in Γ_c^v and Γ_q^v. The representations in parentheses are compatible with the representations labeled by the minus. (b) Point H in Γ_c^v and point Z in Γ_q^v. The representations in parentheses are compatible with the representations labeled by the minus. (c) Points P in Γ_c^v and Γ_q^v. (d) Point N in Γ_c^v and points X and N in Γ_q^v.

(a)

O_h^9	$\Gamma_1(\Gamma_1')$	$\Gamma_2(\Gamma_2')$	$\Gamma_{12}(\Gamma_{12}')$	$\Gamma_{25}'(\Gamma_{25})$	$\Gamma_{15}'(\Gamma_{15})$
C_{4h}^5	$\Gamma_1^\pm$	$\Gamma_2^\pm$	$\Gamma_1^\pm+\Gamma_2^\pm$	$\Gamma_2^\pm+\Gamma_3^\pm+\Gamma_4^\pm$	$\Gamma_1^\pm+\Gamma_3^\pm+\Gamma_4^\pm$
D_{4h}^{17}	$\Gamma_1^\pm$	$\Gamma_3^\pm$	$\Gamma_1^\pm+\Gamma_3^\pm$	$\Gamma_4^\pm+\Gamma_5^\pm$	$\Gamma_2^\pm+\Gamma_5^\pm$

(b)

O_h^9	$H_1(H_1')$	$H_2(H_2')$	$H_{12}(H_{12}')$	$H_{25}'(H_{25})$	$H_{15}'(H_{15})$
C_{4h}^5	$Z_1^\pm$	$Z_2^\pm$	$Z_1^\pm+Z_2^\pm$	$Z_2^\pm+Z_3^\pm+Z_4^\pm$	$Z_1^\pm+Z_3^\pm+Z_4^\pm$
D_{4h}^{17}	$Z_1^\pm$	$Z_3^\pm$	$Z_1^\pm+Z_3^\pm$	$Z_4^\pm+Z_5^\pm$	$Z_2^\pm+Z_5^\pm$

(c)

O_h^9	P_1	P_2	P_3	P_4	P_5
C_{4h}^5	P_1	P_2	P_1+P_2	$P_2+P_3+P_4$	$P_1+P_3+P_4$
D_{4h}^{17}	P_1	P_3	P_1+P_3	P_4+P_5	P_2+P_5

(d)

O_h^9	N_1	N_2	N_3	N_4	N_1'	N_2'	N_3'	N_4'
C_{4h}^5	X_1^+	X_2^+	X_2^+	X_1^+	X_2^-	X_1^-	X_1^-	X_2^-
	N^+	N^+	N^+	N^+	N^-	N^-	N^-	N^-
D_{4h}^{17}	X_1^+	X_2^+	X_4^+	X_3^+	X_2^-	X_1^-	X_3^-	X_4^-
	N_1^+	N_2^+	N_2^+	N_1^+	N_2^-	N_1^-	N_1^-	N_2^-

Table I shows that the Bloch functions with Z_2^+ and P_2 symmetry may form an FM band, namely, band 2 in this table. This band can be connected to Γ_{25}' as well as to Γ_{12} because both states subduce the state Γ_2^+ at the transition from O_h^9 to C_{4h}^5; see Table III. Hence, in both cases the compatibility relations are satisfied in C_{4h}^5. (In this contex, it is meaningless that in O_h^9 the compatibility relations are violated between Γ and P in the first case and between Γ and H in the second case.) We choose Γ_{12} to belong to the FM band in order to get a nearly empty band for the minority-spin states and nearly filled band for the majority-spin states. (It should be noted that also a linear combination of the two Γ_2^+ Bloch functions subduced from Γ_{25}' and Γ_{12} may belong to the FM band.)

According to Tables I and III both the N_1 and N_4 state may belong to the FM band. In Fig. 1 the N_4 state is chosen since N_1 is not connected to Γ_{12} between Γ and N.

VII. DISCUSSION

A. Stability of the ferromagnetic state

Iron possesses a narrow FM band which is nearly empty for the minority-spin states and nearly filled for the majority-spin states, see the preceding Sec. VI and Fig. 1. These findings are interpreted within a nonadiabatic extension of the original Heisenberg model of magnetism, the ''nonadiabatic Heisenberg model.'' The aim of this paper is to report evidence that the FM band causes the stability of the ferromagnetic state in iron.

Also within this new model it is the familiar exchange mechanism which keeps the spins parallel in the ferromagnetic state. However, it is the special symmetry of the FM band which *activates* a spin-dependent exchange mechanism producing the ferromagnetic spin structure. As a consequence of the postulates of the nonadiabatic Heisenberg model, the Coulomb repulsion energy of the electrons of the FM band is lowered by ΔE [given in Eq. (3.1)], if an exchange mechanism operates in iron which produces a ferromagnetic spin structure with the magnetic group *M*. Therefore, the electrons of the FM band modify their orbitals within the nonadiabatic localized states in such a way that the exchange energy E_{ex} is maximum for a spin structure with the group *M*; see Eq. (4.2).

The energy difference E_f between the paramagnetic and the ferromagnetic states is not given by the exchange energy E_{ex} alone, but by

$$E_f = \Delta E + E_{ex};$$

see Sec. IV. Hence, E_f may be positive even if E_{ex} is negative.

From Eq. (4.2) we may conclude that the energetically most favorable exchange mechanism is activated in iron. The nonadiabatic Heisenberg model does not specify this mechanism. Hence, there is no reason to assume that this mechanism is different from the mechanisms commonly considered as decisive for ferromagnetism. However, interatomic exchange coupling in the FM band should be an important part of this exchange mechanism since a maximum number of atoms is occupied by only one electron of the FM band. Hence, there are optimal conditions for a large exchange energy within the FM band.

Within the nonadiabatic Heisenberg model, the electron system is described by the nonadiabatic Hamiltonian H^n given in Eq. (2.10). An important feature of H^n is that it has the correct symmetry of the ferromagnetic state; see Eqs. (3.5), (3.6), and (3.7). Especially, H^n does not commute with the operator K of time inversion.

There is evidence that a Hamiltonian commuting with K does not possess magnetic eigenstates; see Sec. V. For this reason, I presume that any spontaneous magnetic structure in a metal is connected with a narrow, roughly half-filled ''magnetic band'' in the paramagnetic band structure of this metal. In this context, an energy band is called a ''magnetic band'' if the Bloch functions of this band can be unitarily transformed into Wannier functions that are best localized, symmetry adapted to the magnetic group of the considered spin structure, and situated at the atoms.

B. Condition for ferromagnetism

The FM band in iron is characterized by the representations

$$\Gamma_{12}, H'_{25}, N_4, \text{ and } P_3 \tag{7.1}$$

of the paramagnetic point group O_h. In the bcc transition elements, a FM band occurs not so rarely as the antiferromagnetic (AF) band and the superconducting band (σ band) which are proposed to cause the stability of the antiferromagnetic state in chromium[4] and the superconducting state in several transition elements.[3,5]

The AF band of chromium is characterized by the representations

$$\Gamma'_{25}, H'_{25}, N_1, \text{ and } P_3.$$

At the same time, this band forms a FM band. That means, the Bloch functions of this band can be unitarily transformed either into basis functions of the representations

$$\Gamma_3^+, \Gamma_4^+, X_5, M_{20}, A_{10}, Z_{11}, \text{ and } R_5$$

of the space group D_{4h}^6 of the spin density wave[11] or into basis functions of the representations

$$\Gamma_2^+, P_2, X_1^+, Z_2^+, \text{ and } N^+$$

of the space group C_{4h}^5 of the ferromagnetic state (see Appendix A). Thus, within the nonadiabatic Heisenberg model, chromium may either have an antiferromagnetic or a ferromagnetic ground state. Obviously, the antiferromagnetic state is energetically more favorable than the ferromagnetic state.

The same statement applies to the σ band in the bcc transition elements,

$$\Gamma'_{25}, H'_{25}, N_2, \text{ and } P_4,$$

which is also a FM band. Thus, a metal with a half-filled σ band like niobium may either have a ground state with spin-phonon interaction (which, at low temperatures, produces a superconducting state) or a ferromagnetic state. Obviously, also the state with spin-phonon interaction is energetically more favorable than the ferromagnetic state.

The Γ_{12} state in the FM band of iron belongs neither to any AF nor to any σ band. Hence, the electrons of this band have no other possibility but to form a ferromagnetic state in order that their Coulomb repulsion energy is lowered by ΔE.

On the basis of these findings I may give a provisional condition for ferromagnetism: a metal may have a stable ferromagnetic ground state if, first, one of its narrowest, partly filled paramagnetic energy bands is a FM band and if, second, this band is neither an AF nor a σ band.

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APPENDIX A: WANNIER FUNCTIONS OF THE FERROMAGNETIC BAND

The magnetic group of ferromagnetic iron,

$$M = I4/mm'm', \tag{A1}$$

may be written as

$$M = G + K\{C_{2x}|\vec{0}\}G \tag{A2}$$

if the magnetic moments point in the z direction. K is the operator of time inversion, C_{2x} denotes a rotation about the x axis through the angle π, $\{C_{2x}|\vec{0}\}$ is a symmetry operation [cf. Eq. (A11)], and

$$G = I4/m = C_{4h}^5 \tag{A3}$$

is the space group of the magnetic state. The point group

$$M_0 = 4/mm'm' \tag{A4}$$

of M has the form

$$M_0 = G_0 + KC_{2x}G_0, \tag{A5}$$

where

$$G_0 = 4/m = C_{4h} \tag{A6}$$

is the point group of G. Both groups M and G have the tetragonal Brillouin zone Γ_q^v.

The ferromagnetic group M is a subgroup of the paramagnetic group

$$M^P = O_h^9 + KO_h^9 \tag{A7}$$

of bcc iron. Furthermore, in this paper the ‘‘magnetic overgroup’’

$$M' = M + KM \tag{A8}$$

of M is considered. M' may be written as

$$M' = D_{4h}^{17} + KD_{4h}^{17} \tag{A9}$$

and, hence, has the tetragonal point group

$$M_0' = D_{4h} + KD_{4h}. \tag{A10}$$

The elements

$$a = \{\alpha|\vec{R}\} \tag{A11}$$

of G consist of a point group operation α and a primitive translation $\vec{R}$. The symmetry operators $P(a)$ and the operator K of time inversion act on a function of position, $f(\vec{r})$, according to

$$P(a)f(\vec{r}) = f(\alpha^{-1}\vec{r} - \alpha^{-1}\vec{R}) \tag{A12}$$

and

$$Kf(\vec{r}) = f^*(\vec{r}), \tag{A13}$$

respectively.

Consider the band structure of Fe depicted in Fig. 1, in particular the FM band denoted by the heavy lines. The Bloch functions of this band in paramagnetic iron shall be unitarily transformed into Wannier functions

$$w(\vec{r} - \vec{T}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}}^{BZ} e^{-i\vec{k}\cdot\vec{T}} g(\vec{k}) \varphi_{\vec{k}}(\vec{r}), \tag{A14}$$

which are situated at the lattice points $\vec{T}$. The sum runs over the N wave vectors $\vec{k}$ of the Brillouin zone (BZ) and $g(\vec{k})$ denotes a $\vec{k}$-dependent phase factor with $|g(\vec{k})| = 1$.

The FM band is characterized by the representations

$$\Gamma_{12}, H_{25}', N_4, \text{ and } P_3, \tag{A15}$$

of O_h^9. These representations subduce representations of $G = C_{4h}^5$ according to

$$\Gamma_{12} \to \Gamma_1^+ + \Gamma_2^+, \quad P_3 \to P_1 + P_2, \quad N_4 \to X_1^+,$$

$$H_{25}' \to Z_2^+ + Z_3^+ + Z_4^+, \quad N_4 \to N^+; \tag{A16}$$

see Table III. Hence, at the points of symmetry Γ, P, X, Z, and N of Γ_q^v the Bloch functions of the FM band may be chosen in such a way that they are basis functions of the representations

$$\Gamma_2^+, P_2, X_1^+, Z_2^+, \text{ and } N^+,$$

respectively, of band 2 in Table I. Consequently,[6,7] the phase factor $g(\vec{k})$ in Eq. (A14) may be chosen in such a way that the Wannier functions are (1) best localized and (2) symmetry adapted to G according to

$$P(a)\langle\vec{r}|\vec{T}\rangle = d(\alpha)\langle\vec{r}|\vec{T}'\rangle \quad \text{for} \quad a \in G, \tag{A17}$$

with the abbreviations

$$\langle\vec{r}|\vec{T}\rangle = w(\vec{r} - \vec{T}) \tag{A18}$$

and

$$\vec{T}' = \alpha\vec{T} + \vec{R}. \tag{A19}$$

The c numbers $d(\alpha) = \pm 1$ are the representatives of Γ_2^+.

The corepresentation $D\Gamma_2^+$ of M derived from Γ_2^+ is one dimensional, too; see Table 7.15 of Ref. 10. Therefore,[8,11] the phase factor $g(\vec{k})$ even can be chosen in such a way that the Wannier functions are symmetry adapted to the complete magnetic group M. Hence, in addition to Eq. (A17) we have

$$KP(a)\langle\vec{r}|\vec{T}\rangle = d(K\alpha)\langle\vec{r}|\vec{T}'\rangle \quad \text{for} \quad a \in \{C_{2x}|\vec{0}\}G, \tag{A20}$$

with again $\vec{T}'$ being given by Eq. (A19). The c numbers $d(K\alpha) = \pm 1$ are representatives of $D\Gamma_2^+$.

The Bloch functions of the bands listed in Table II can be unitarily transformed into best localized Wannier functions which are symmetry adapted to the magnetic overgroup M' given by Eqs. (A8) and (A9). The representations (A15) of the FM band subduce representations

$$\Gamma_{12} \to \Gamma_1^+ + \Gamma_3^+, \quad P_3 \to P_1 + P_3, \quad N_4 \to X_3^+,$$

$$H_{25}' \to Z_4^+ + Z_5^+, \quad N_4 \to N_1^+, \tag{A21}$$

of D_{4h}^{17}; see Table III. Table II shows that neither of the two bands (in the third and fourth rows of this table) related to band 2 is compatible with the symmetry of the FM band since P_3 and Z_4^+ do not belong to the same band in Table II. Therefore, $g(\vec{k})$ cannot be chosen in such a manner that Eqs. (A17), (A20), and $K\langle\vec{r}|\vec{T}\rangle = c\langle\vec{r}|\vec{T}\rangle$ (with $|c| = 1$) are satisfied at the same time. Hence we have

$$K\langle\vec{r}|\vec{T}\rangle \neq c\langle\vec{r}|\vec{T}\rangle \tag{A22}$$

(with $|c| = 1$), since we assume that Eqs. (A17) and (A20) are satisfied.

Applying K on both sides of Eq. (A14), we see that the functions $Kw(\vec{r} - \vec{T})$ are a unitary transformation of the time-inverted Bloch functions $K\varphi_{\vec{k}}(\vec{r})$. Because the Bloch functions are eigenfunctions of the real Hartree-Fock Hamiltonian, always both $K\varphi_{\vec{k}}(\vec{r})$ and $\varphi_{\vec{k}}(\vec{r})$ belong to the FM band. Hence, the time-inverted Wannier functions $Kw(\vec{r} - \vec{T})$ as well as the Wannier functions $w(\vec{r} - \vec{T})$ form a basis in the space spanned by the Bloch functions of the FM band. Consequently, the functions $Kw(\vec{r} - \vec{T})$ may be written as linear combinations

$$K\langle\vec{r}|\vec{T}\rangle = \sum_{\vec{T}'} \langle\vec{T}'|K|\vec{T}\rangle\langle\vec{r} \ \ |\vec{T}'\rangle \tag{A23}$$

of the Wannier functions $w(\vec{r} - \vec{T})$, with

$$\sum_{\vec{T}'} |\langle\vec{T}'|K|\vec{T}\rangle|^2 = 1 \tag{A24}$$

and at least two nonvanishing coefficients $\langle\vec{T}_1|K|\vec{T}\rangle$ and $\langle\vec{T}_2|K|\vec{T}\rangle$.

Equations (A17), (A20), and (A23) also may be written for the fermion operators $c^{\dagger}_{\vec{T}s}$ in Eq. (2.2),

$$P(a)c^{\dagger}_{\vec{T}s}P^{-1}(a)=d(\alpha)c^{\dagger}_{\vec{T}'s}\quad\text{for}\quad a\in G,\tag{A25}$$

$$KP(a)c^{\dagger}_{\vec{T}s}P^{-1}(a)K^{-1}=d(K\alpha)c^{\dagger}_{\vec{T}'s}\quad\text{for}\quad a\in\{C_{2x}|\vec{0}\}G,\tag{A26}$$

with $|d(\alpha)|=|d(K\alpha)|=1$ and

$$Kc^{\dagger}_{\vec{T}s}K^{-1}=\sum_{\vec{T}'}\langle\vec{T}'|K|\vec{T}\rangle c^{\dagger}_{\vec{T}'s},\tag{A27}$$

with at least two nonvanishing summands.

APPENDIX B: NONADIABATIC LOCALIZED FUNCTIONS OF THE FERROMAGNETIC BAND

In this section the properties of the nonadiabatic localized functions of the FM band will be given as far as they are determined within the nonadiabatic Heisenberg model. From these properties, the important equation (B21) will be derived.

Each localized state $|\vec{T}\rangle$ represented by the Wannier functions $w(\vec{r}-\vec{T})$ given by Eq. (A18) may be occupied by an electron with spin-down or spin-up direction. We put

$$\langle\vec{r},t|\vec{T},s\rangle=\langle\vec{r}|\vec{T}\rangle u_s(t),\tag{B1}$$

where

$$u_s(t)=\delta_{st}\tag{B2}$$

stands for Pauli's spin functions with the spin quantum number $s=\pm\frac{1}{2}$ and the spin coordinate $t=\pm\frac{1}{2}$. A symmetry operator $S(\alpha)$ of the three-dimensional rotation group $O(3)$ acts on $u_s(t)$ according to[10]

$$S(\alpha)u_s(t)\equiv u_s(\alpha^{-1}t)=\sum_{s'}d_{s's}(\alpha)u_{s'}(t)\quad\text{for}\quad\alpha\in O(3),\tag{B3}$$

where the matrices $[d_{s's}(\alpha)]$ are the representatives of the two-dimensional double-valued representation $D_{1/2}$ of $O(3)$. The matrices $[d_{s's}(\alpha)]$ may be chosen diagonal for $\alpha\in G_0$ and are assumed to be diagonal. In this case, the spin lies in z direction.

The effect of the time inversion operator K is given by

$$Ku_s(t)=g_s u_{-s}(t),\tag{B4}$$

with[12]

$$g_{\pm 1/2}=\mp i.\tag{B5}$$

The localized functions $\langle\vec{r},t|\vec{T},s\rangle$ are replaced by nonadiabatic localized functions,

$$\langle\vec{r},t|\vec{T},s\rangle\rightarrow\langle\vec{r},t,\vec{q}\ \ |\vec{T},m,\nu\rangle,\tag{B6}$$

which are orthonormal according to

$$\begin{aligned}\langle\vec{T}',m',\nu'|\vec{T},m,\nu\rangle&\\ &\equiv\sum_t\iint\langle\vec{T}',m',\nu'|\vec{r},t,\vec{q}\rangle\langle\vec{r},t,\vec{q}|\vec{T},m,\nu\rangle d\vec{r}d\vec{q}\\ &=\delta_{\vec{T}'\vec{T}}\delta_{m'm}\delta_{\nu'\nu}.\end{aligned}\tag{B7}$$

The quantum number $\nu=n$ labels the functions satisfying Eqs. (2.13) and (4.2). In principle, n may depend on m or $\vec{T}$. Equations (B11) and (B12) show that n may take two different values n_1 and n_2,

$$n=\begin{cases}n_1 & \text{for}\quad m=\frac{1}{2},\\ n_2 & \text{for}\quad m=-\frac{1}{2},\end{cases}\tag{B8}$$

since the two sets of functions belonging to n_1 and n_2, respectively, are not connected by symmetry. For instance, n_1 might belong to a moderate and n_2 to a more heavy motion of the center of mass. In the following, n is given by Eq. (B8) and ν may take the two values n_1 and n_2 independently of m.

From Eqs. (3.5) and (3.6) it follows that the nonadiabatic localized functions have the same symmetry as the adiabatic functions. However, the symmetry operators $P(a)$ now act on $\vec{r},t$, and on the new coordinate $\vec{q}$ according to

$$\begin{aligned}P(a)&\langle\vec{r},t,\vec{q}|\vec{T},m,\nu\rangle\\ &=\langle\alpha^{-1}\vec{r}-\alpha^{-1}\vec{R},\alpha^{-1}t,\alpha^{-1}\vec{q}|\vec{T},m,\nu\rangle,\end{aligned}\tag{B9}$$

and the application of K yields

$$K\langle\vec{r},t,\vec{q}|\vec{T},m,\nu\rangle=g_s\langle\vec{r},t,\vec{q}|\vec{T},-m,\nu\rangle^*.\tag{B10}$$

Suppressing from now on the $\langle\vec{r},t,\vec{q}|$ representation, from Eqs. (A17), (A20), and (B3) we get

$$P(a)|\vec{T},m,n\rangle=d_m(\alpha)|\vec{T}',m,n\rangle\quad\text{for}\quad a\in G\tag{B11}$$

and

$$KP(a)|\vec{T},m,n\rangle=d_m(K\alpha)|\vec{T}',m,n\rangle,\quad\text{for}\quad a\in\{C_{2x}|\vec{0}\}G,\tag{B12}$$

with T' being given in Eq. (A19). All the c numbers $d_m(\alpha)$ and $d_m(K\alpha)$ have the absolute value 1,

$$|d_m(\alpha)|=|d_m(K\alpha)|=1,\tag{B13}$$

since they are the representatives of the two one-dimensional corepresentations (related to $m=\pm\frac{1}{2}$) subduced by the corepresentation $D_{1/2}\times D\Gamma^+_2$ of M_0.

Like the adiabatic localized states, the nonadiabatic localized states $|\vec{T},m,\nu\rangle$ arise by a unitary transformation from nonadiabatic Bloch states $|\vec{k},m,\nu\rangle$ forming a single (with $m=\pm\frac{1}{2}$ doubly degenerate) energy band labeled by ν. As in the adiabatic case, the nonadiabatic Bloch functions are eigenfunctions of a real operator. Hence, always both, $|\vec{k},m,\nu\rangle$ and $K|\vec{k},m,\nu\rangle$ belong to the same band ν. Thus, the states $K|\vec{T},m,\nu\rangle$ are linear combinations of the states

$|\vec{T}',m',\nu\rangle$ with $m'=-m$ as a consequence of Eq. (B10). The adiabatic equations (A23) and (A24) now may be written as

$$K|\vec{T},m,\nu\rangle=\sum_{\vec{T}'\nu'}|\vec{T}',-m,\nu'\rangle\langle\vec{T}',-m,\nu'|K|\vec{T},m,\nu\rangle, \tag{B14}$$

with

$$\sum_{\vec{T}'}|\langle\vec{T}',-m,\nu|K|\vec{T},m,\nu\rangle|^2=1 \tag{B15}$$

and

$$\langle\vec{T}',-m,\nu'|K|\vec{T},m,\nu\rangle=0 \tag{B16}$$

for $\nu'\neq\nu$ as a consequence of the orthogonality relation (B7).

Let

$$F_{\mathcal{A}}=\sum_{\vec{T}m}|\vec{T},m,n\rangle\langle\vec{T},m,n| \tag{B17}$$

be the operator projecting on the space $\mathcal{A}$ spanned by the states $|\vec{T},m,n\rangle$. That means that $\mathcal{A}$ consists of the nonadiabatic states satisfying Eqs. (2.13) and (4.2). These states belong to the two different bands n_1 and n_2 for $m=+\frac{1}{2}$ and $m=-\frac{1}{2}$, respectively. The states $F_{\mathcal{A}}K|\vec{T},m,n\rangle$ may be written as

$$F_{\mathcal{A}}K|\vec{T},m,n\rangle=\sum_{\vec{T}'}|\vec{T}',-m,n\rangle\langle\vec{T}',-m,n|K|\vec{T},m,n\rangle; \tag{B18}$$

see Eq. (B10). From Eqs. (B8) and (B16) it follows that all the coefficients in Eq. (B18) vanish,

$$\langle\vec{T}',-m,n|K|\vec{T},m,n\rangle=0, \tag{B19}$$

if (and only if) $n_1\neq n_2$. Hence, we have

$$K|\vec{T},m,n\rangle\notin\mathcal{A} \tag{B20}$$

if $n_1\neq n_2$.

The important (see Sec. III B) equation (B20) also may be written for the nonadiabatic fermion operators in Eq. (2.11),

$$Kc^{n\dagger}_{\vec{T}m}K^{-1}\notin\mathcal{A} \tag{B21}$$

if $n_1\neq n_2$, where here $\mathcal{A}$ is defined by the projection operator

$$F_{\mathcal{A}}=\sum_{\vec{T}m}c^{n\dagger}_{\vec{T}m}c^{n}_{\vec{T}m}. \tag{B22}$$

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[1] W. Heisenberg, Z. Phys. **49**, 619 (1928).

[2] J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).

[3] E. Krüger, Phys. Rev. B **30**, 2621 (1984).

[4] E. Krüger, Phys. Rev. B **40**, 11 090 (1989).

[5] E. Krüger (unpublished).

[6] E. Krüger, Phys. Status Solidi B **52**, 215 (1972).

[7] E. Krüger, Phys. Status Solidi B **52**, 519 (1972).

[8] E. Krüger, Phys. Status Solidi B **61**, 193 (1974).

[9] N.F. Mott, Can. J. Phys. **34**, 1356 (1956).

[10] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Claredon, Oxford, 1972).

[11] E. Krüger, Phys. Rev. B **36**, 2263 (1987).

[12] H.-W. Streitwolf, *Gruppentheorie in der Festkörperphysik* (Akademische Verlagsgesellschaft Geest & Portig KG, Leipzig, 1967).

[13] L.P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[14] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1965), Vol. 2.

[15] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1963).

[16] J. Callaway and C.S. Wang, Phys. Rev. B **16**, 2095 (1977).