Superconductivity interpreted as \( \vec{k} \)-space magnetism

Ekkehard Krüger

Max-Planck-Institut für Metallforschung, D-70506 Stuttgart, Germany

(Dated: November 13, 2018)

In preceding papers\(^1\) a new mechanism of Cooper pair formation was proposed that operates in narrow partly filled “superconducting” energy bands of special symmetry and shows resemblances, and also great differences as compared with the familiar BCS mechanism. In the present paper the resulting superconducting state is interpreted as a state in which the spins are ordered within the \( \vec{k} \) space. In this picture, the peculiar features of the new mechanism, as compared with the BCS mechanism, can be understood in a straightforward manner. On the one hand, the new mechanism resembles the BCS picture, because the formation of Cooper pairs is still mediated by bosons (having dominant phonon character in the isotropic lattices of the conventional superconductors). On the other hand, however, the pair formation is not the result of an attractive electron-electron interaction mediated by these bosons. Rather, the bosons carry the crystal-spin angular momentum \( 1 \cdot \hbar \) and generate in a new way constraining forces that constrain the electrons to form Cooper pairs. The scale of the transition temperatures in conventional and high-temperature superconductors is set by the excitation energies of stable crystal-spin-1 bosons that are different in isotropic and anisotropic materials.

Keywords: occurrence of superconductivity; narrow bands; Heisenberg model; group theory.

1. INTRODUCTION

In previous papers\(^2\) a new mechanism of Cooper pair formation was proposed that operates in narrow partly filled “superconducting” energy bands (\( \sigma \) bands) of special symmetry. Except for their name, these \( \sigma \) bands have no resemblances or analogies with graphite-like \( \sigma \) bands. The new mechanism can be derived within a nonadiabatic extension of the Heisenberg model of magnetism\(^6\) the “nonadiabatic Heisenberg model” (NHM) described in detail in Ref.\(^7\). The NHM emphasizes in a new way the atomiclike character of the electrons in narrow bands as described by Mot\(^1\) and Hubbard\(^2\); the electrons occupy the localized states as long as possible and perform their band motion by hopping from one atom to another. Within the NHM these localized states are represented by (spin-dependent) Wannier functions which form an exactly unitary transformation of the Bloch functions of the considered energy bands.

The new mechanism of Cooper pair formation resembles the familiar mechanism presented within the Bardeen-Cooper-Schrieffer (BCS) theory\(^3\) because the formation of Cooper pairs is still mediated by bosons. In contrast to the BCS mechanism, however, these bosons carry the crystal spin \( 1 \cdot \hbar \) and must be sufficiently stable to transport it through the crystal. Further, the formation of Cooper pairs is not the result of an attractive electron-electron interaction but is constrained in a new way by quantum mechanical constraining forces operating in \( \sigma \) bands.

These constraining forces have been illustrated in Ref.\(^8\) in terms of “spring-mounted” Cooper pairs. In the present paper we interpret the superconducting state within a narrow \( \sigma \) band as “\( \vec{k} \)-space magnetism”. This new form of magnetism complies with the conservation law of spin angular momentum only if the electrons form Cooper pairs. Within this picture, the essential features of the new mechanism of Cooper pair formation as given in the preceding paragraph can be clearly understood.

A set of energy bands of a metal is called \( \sigma \)-band complex if the Bloch functions belonging to this set can be unitarily transformed into spin-dependent Wannier functions (spin-dependent WFs) which are best localized, symmetry adapted to the paramagnetic group of this metal and situated at the atoms.\(^1\) A \( \sigma \)-band complex contains just as many bands as there are atoms in the unit cell. However, only those atoms must be considered which are responsible for the superconducting state.

For simplicity, in this paper we assume the \( \sigma \)-band complex to consist of a single band. The spin-dependent WFs of such a single \( \sigma \) band are shortly defined in Section\(^9\) and, more detailed, in Refs.\(^2\) or\(^7\). Within the NHM, the peculiar properties of the spin-dependent WFs lead to a special operator \( H^\sigma_{Cb} \) of Coulomb interaction shortly described in Section\(^8\). The interaction \( H^\sigma_{Cb} \) is proposed to be responsible for superconductivity.

In Section\(^8\) \( H^\sigma_{Cb} \) is approximated by a purely electronic operator \( H^\sigma_{Cb} \), and in Section\(^8\) \( H^\sigma_{Cb} \) is interpreted as a magnetic interaction that produces a spin structure in the \( \vec{k} \) space. Within this spin structure, however, electronic scattering processes violate the conservation of spin angular momentum. As shown in the following Section\(^8\), the spin structure is stable if the electrons form Cooper pairs coupled via crystal-spin-1 bosons.

2. SPIN-DEPENDENT WANNIER FUNCTIONS

Consider a metal with one atom in the unit cell and assume that this metal possesses a narrow, half-filled \( \sigma \) band in its calculated band structure.

The Bloch functions \( \varphi_{\vec{k}}(\vec{r}) \) of this band can be unitarily
transformed into spin-dependent WFs

\[ w_m(\vec{r} - \vec{T}, t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i \vec{k} \cdot \vec{r}} \phi_{\vec{k}m}(\vec{r}, t) \]  \hspace{1cm} (1)

with the functions

\[ \phi_{\vec{k}m}(\vec{r}, t) = \sum_{s = -\frac{1}{2}}^{+\frac{1}{2}} f_{sm}(\vec{k}) u_s(t) \phi_\vec{k}(\vec{r}) \]  \hspace{1cm} (2)

being “spin-dependent Bloch functions” with spin directions depending on the wave vector \( \vec{k} \). The two-dimensional matrix

\[ f(\vec{k}) = [f_{sm}(\vec{k})] \] \hspace{1cm} (3)

is, for each \( \vec{k} \), unitary and

\[ u_s(t) = \delta_{st} \] \hspace{1cm} (4)

stands for Pauli’s spin function with the spin quantum number \( s = \pm \frac{1}{2} \) and the spin coordinate \( t = \pm \frac{1}{2} \).

The quantum number \( m = \pm \frac{1}{2} \) of the crystal spin distinguishes between the two Wannier functions belonging to the same position \( \vec{T} \). If in Eq. (2) we have

\[ f_{sm}(\vec{k}) = \delta_{sm}, \] \hspace{1cm} (5)

the two functions \( \phi_{\vec{k}m}(\vec{r}, t) \) with \( m = \pm \frac{1}{2} \) are usual Bloch functions with the spins lying in \(+z\) and \(-z\) direction, respectively. Otherwise, these functions still are usual Bloch functions with antiparallel spins that lie, however, in a direction \( z' \) different from the \( z \) direction.

In a \( \sigma \) band the matrix \( f(\vec{k}) \) in Eq. (3) can be chosen in such a way that

1. the spin-dependent Bloch functions \( \phi_{\vec{k}m}(\vec{r}, t) \) vary smoothly through the whole \( \vec{k} \) space, and
2. the \( w_m(\vec{r} - \vec{T}, t) \) are adapted to the symmetry of the considered metal.

In particular, by application of the operator \( K \) of time inversion we obtain

\[ Kw_m(\vec{r} - \vec{T}, t) = \pm w_{-m}(\vec{r} - \vec{T}, t) \] \hspace{1cm} (6)

(where the plus is defined to belong to \( m = +\frac{1}{2} \) and the minus to \( m = -\frac{1}{2} \)). The smoothness of the spin-dependent Bloch functions \( \phi_{\vec{k}m}(\vec{r}, t) \) guarantees that the spin-dependent WFs are optimally localizable.

It is essential that in a \( \sigma \) band the matrix \( f(\vec{k}) \) is not independent of \( \vec{k} \) if the WFs comply with the above conditions (1) and (2).  

3. SPIN-BOSON INTERACTION

The nonadiabatic Coulomb interaction

\[ H_{Cb}^{\sigma} = \sum_{\vec{T}, m} \langle \vec{T}'', l_1; \vec{T}''', l_2; \vec{T}, m_1, n; \vec{T}_1, m_1, n; \vec{T}_2, m_2, n | H_{Cb} | \vec{T}', l_1; \vec{T}_1', m_1, n; \vec{T}_2', m_2, n \rangle b_{\vec{T}''l_1}^\dagger b_{\vec{T}''', l_2}^\dagger c_{\vec{T}_1 m_1}^n c_{\vec{T}_2 m_2}^n + H.c. \] \hspace{1cm} (7)

in a narrow half-filled \( \sigma \) band depends also on boson operators \( b_{\vec{T}l}^\dagger \) and \( b_{\vec{T}l} \) in order that it conserves the total crystal spin,

\[ [H_{Cb}^{\sigma}, M(\alpha)] = 0 \]  \hspace{1cm} for \( \alpha \in G_0, \] \hspace{1cm} (8)

see Ref. 3. The symmetry operators \( M(\alpha) \) of the crystal spin are defined for the electrons in Ref. 3 and for the bosons in Ref. 4. \( G_0 \) denotes the point group. The fermion operators \( c_{\vec{T}m}^n \) and \( c_{\vec{T}m}^n \) create and annihilate electrons with crystal spin \( m \) in the nonadiabatic localized states \( | \vec{T}, m, n \rangle \) and the boson operators \( b_{\vec{T}l}^\dagger \) and \( b_{\vec{T}l} \) create and annihilate localized bosons \( | \vec{T}, l \rangle \) (with the crystal spin \( l = -1, 0, +1 \)) which are sufficiently stable to transport crystal spin angular momenta through the crystal.

The nonadiabatic states \( | \vec{T}, m, n \rangle \) are represented by nonadiabatic localized functions of the form

\[ \langle \vec{r}, t, \vec{q}, | \vec{T}, m, n \rangle \], where the new coordinate \( \vec{q} \) stands for that part of the motion of the center of mass of the localized state \( | \vec{T}, m, n \rangle \) which nonadiabatically follows the motion of the electron occupying this state. We may imagine that \( \vec{q} \) denotes the acceleration of the center of mass.

4. STATIC APPROXIMATION WITHIN THE NONADIABATIC HEISENBERG MODEL

Assume the atomic cores in the considered crystal to be rigid and absolutely immovable. On this fixed atomic
array we approximate the operator $H_{Cb}^{st}$ by the operator

$$H_{Cb}^{st} = \sum_{T,m}(\hat{T}_1, m_1; \hat{T}_2, m_2)|H_{Cb}|\hat{T}_1, m_1; \hat{T}_2, m_2\rangle \times c_{\hat{T}_1 m_1}^\dagger c_{\hat{T}_2 m_2}^\dagger c_{\hat{T}_2 m_2} c_{\hat{T}_1 m_1}$$

(9)

not depending on boson operators and, nevertheless, conserving the crystal spin,

$$[H_{Cb}^{st}, M(\alpha)] = 0 \text{ for } \alpha \in G_0.$$  

(10)

The fermion operators $c_{\hat{T}_m}^\dagger$ and $c_{\hat{T}_m}$ create and annihilate electrons in localized states $|\hat{T}, m\rangle$ which no longer depend on $n$ and, hence, are represented by the spin-dependent WFs $w_n(\hat{r} - \hat{T}, t)$.

$H_{Cb}^{st}$ commutes with the space group operators because the $w_n(\hat{r} - \hat{T}, t)$ are adapted to the symmetry of the considered metal. In particular, from Eq. (9) it follows that $H_{Cb}^{st}$ commutes with the operator $K$ of time inversion,

$$[H_{Cb}^{st}, K] = 0.$$  

(11)

As a consequence of Eq. (10), $H_{Cb}^{st}$ does not conserve the electron spin $s$, see the following Section 6. Therefore, this “static approximation” within the NHM differs from the familiar adiabatic approximation. It is the natural approximation that ignores the motion of the atomic cores when we start from the NHM.

5. THE STATIC GROUND STATE WITHIN A NARROW $\sigma$ BAND

Let $E^{st}$ be the electron system of a narrow, half-filled $\sigma$ band represented by the static operator

$$H^{st} = H_{HF} + H_{Cb}^{st}$$

(12)

(where $H_{HF}$ stands for the Hartree-Fock operator). In $E^{st}$ the crystal spin $m$ of the spin-dependent Bloch functions $\phi_{km}(\hat{r}, t)$ given in Eq. (6) is a conserved quantity. Consequently, at any scattering process of two Bloch electrons in $E^{st}$ the spin directions of the scattered electrons are (slightly) changed. This leads to a ground state $|G^{st}\rangle$ in which the Bloch states $|\hat{k}m\rangle$ have $\hat{k}$-dependent spin directions as determined by the two-dimensional unitary matrix $f(\hat{k})$ in Eq. (4). (It should be noted that the crystal spin $m$ and the spin $s$ without the addition “crystal” are different. The former denotes the crystal spin of the nonadiabatic localized states and the bosons, and the latter the spin of the naked electrons.)

The matrix $f(\hat{k})$ varies smoothly as a function of $\hat{k}$. It determines the symmetry and (sensitively) the localization of the spin-dependent WFs. Both their symmetry and their localization have an important physical meaning within the NHM: The WFs must be adapted to the symmetry of the considered metal in order that the nonadiabatic Hamiltonian commutes with the operators of the space group. Further, the WFs must be optimally localized in order that the Coulomb energy in the $\sigma$ band is as low as possible. Strictly speaking, the WFs are “optimally” localized if the energy difference $\Delta E$ in Eq. (2.20) of Ref. 4 is maximum, see the detailed description of the NHM in Ref. 8.

Hence, the directions $z'$ of the electron spins are fixed in $|G^{st}\rangle$ by the condition that the Coulomb energy is minimum. Therefore, we interpret the interaction $H_{Cb}^{st}$ as “magnetic” spin-spin interaction that produces Bloch states with $\hat{k}$-dependent spin directions $z'$. However, the state $|G^{st}\rangle$ differs to some aspects from a magnetic state in the local space: First, $|G^{st}\rangle$ is invariant under time inversion,

$$K|G^{st}\rangle = |G^{st}\rangle,$$  

(13)

since $H^{st}$ commutes with $K$. (Any magnetic order in the local space is not invariant under time inversion. Within the NHM, such a state exists only if the nonadiabatic Hamiltonian $H^n$ does not commute with $K$, too.) Second, the spins are not ordered in the sense that the spins of the Bloch states have only one direction, say $+z'$ direction, but the spins may either lie in $+z'$ or in $-z'$ direction with only the $z'$ direction being fixed. Therefore, this new magnetic interaction generating the $\hat{k}$-dependent $z'$ direction of the spins cannot be calculated by exchange integrals and, hence, should not be called “exchange interaction”. Thirdly, the pure magnetic state $|G^{st}\rangle$ is not realized in nature, see the following Section 6.

6. COOPER PAIR FORMATION IN A NARROW $\sigma$ BAND

Starting from the magnetic state $|G^{st}\rangle$ we may understand in a straightforward way the formation of Cooper pairs within the NHM.

At any scattering process in the electron system $E^{st}$ the total electron spin of the scattered electrons is not conserved. Hence, the electrons must interchange spin angular momenta with the lattice of the atomic cores. Such a mechanism produces deformed and accelerated atomic cores and cannot be understood within the static approximation. Rather it is described by the nonadiabatic Coulomb interaction $H_{Cb}^{st}$ representing a system in which at any electronic scattering process two crystal-spin-1 bosons are excited or absorbed.

We may assume that at zero temperature the crystal-spin-1 bosons are only virtually excited. That means that each boson pair is reabsorbed immediately after its generation. Hence, whenever a boson pair is excited during a certain scattering process

$$\hat{k}_1, \hat{k}_2 \rightarrow \hat{k}_1, \hat{k}_2$$

(14)

of two electrons, this boson pair must be reabsorbed immediately after its generation during a second scattering
process
\[ \vec{k}'_1, \vec{k}'_2 \rightarrow \vec{k}_3, \vec{k}_4 \] (15)
of two other electrons.

Such a state can be studied within \( \mathcal{E}^{st} \). Here we must look for scattering processes
\[ \vec{k}'_1, \vec{k}'_2, \vec{k}'_3, \vec{k}'_4 \rightarrow \vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4 \] (16)
conserving the total electron spin. Only in this case, the boson pair created during the first process (21) is reabsorbed during the second process (15).

At first sight, such scattering processes seem not to exist in \( \mathcal{E}^{st} \) because the matrix \( f(\vec{k}) \) cannot be chosen independent of \( \vec{k} \) in a \( \sigma \) band. However, from Eq. (6) the equation
\[ f_{sm}(\vec{k}) = \pm f^*_{s,-m}(\vec{k}) \] (17)
may be derived, showing that the spins in the Bloch state \( |\vec{k}m\rangle \) and in its time-inverted state \( |-\vec{k} - m\rangle \) lie exactly opposite.

Thus, in \( \mathcal{E}^{st} \) we can construct (symmetrized) Cooper pairs
\[ \beta^\dagger_{\vec{k}} = c^\dagger_{\vec{k} \uparrow} c^\dagger_{\vec{k} \downarrow} - c^\dagger_{\vec{k} \downarrow} c^\dagger_{\vec{k} \uparrow} \] (18)
with (exactly) zero total spin, where the fermion operators \( c^\dagger_{\vec{k}s} \) create Bloch electrons with spin \( s = \uparrow, \downarrow \). Consequently, scattering processes of the form
\[ \vec{k}', -\vec{k}' \rightarrow \vec{k}, -\vec{k} \] (19)
conservate the total spin angular momentum within \( \mathcal{E}^{st} \).

We now may construct the nonadiabatic state in a narrow half-filled \( \sigma \) band in which any boson pair is reabsorbed immediately after its creation.

Assume all the \( N \) electrons (with \( N \) being even) in \( \mathcal{E}^{st} \) to form Cooper pairs. Consequently, the total electron spin in \( \mathcal{E}^{st} \) is exactly zero. Two of these Cooper pairs we denote by
\[ (\vec{k}'_1, -\vec{k}'_1) \text{ and } (\vec{k}'_2, -\vec{k}'_2). \] (20)

Assume further the two Bloch electrons with wave vectors \( \vec{k}'_1 \) and \( \vec{k}'_2 \) to be scattered into the states \( \vec{k}_1 \) and \( \vec{k}_2 \),
\[ \vec{k}'_1, \vec{k}'_2 \rightarrow \vec{k}_1, \vec{k}_2. \] (21)
After this process the total spin angular momentum in \( \mathcal{E}^{st} \) is no longer zero since the two Cooper pairs (20) are destroyed. Hence, a boson pair was emitted during this scattering process. It may be reabsorbed during a subsequent scattering process if then the total spin in \( \mathcal{E}^{st} \) again is zero, that means, if then all the electrons in \( \mathcal{E}^{st} \) again form Cooper pairs. Thus, at zero temperature, the process
\[ -\vec{k}'_1, -\vec{k}'_2 \rightarrow -\vec{k}_1, -\vec{k}_2 \] (22)
follows immediately upon the first process (21).

7. CONCLUSIONS

The picture of superconductivity as \( \vec{k} \)-space magnetism presented in this paper shows clearly the peculiar feature of the Cooper pair formation within the NHM: Within the NHM any attractive electron-electron interaction is unimportant for the formation of Cooper pairs. The bosons (belonging to the interaction \( H_{\text{inter}} \)) need not effect an attractive interaction between the electrons, but only produce constraining forces that constrain the electrons to form Cooper pairs.

As in Ref. 8, the Cooper pairs generated by these constraining forces in a narrow \( \sigma \) band can be illustrated in terms of “spring-mounted” Cooper pairs, cf. Fig. 3 in Ref. 8. Let \( \mathcal{P}^0 \) be the subspace of the Hilbert space spanned by the \( N \)-electron states in the \( \sigma \) band in which all the electrons form Cooper pairs, and assume all the electrons to be in \( \mathcal{P}^0 \). Whenever two electrons are scattered out of \( \mathcal{P}^0 \), a boson pair is excited which can only be reabsorbed when the electrons are scattered in such a way that again they lie in \( \mathcal{P}^0 \). Hence, the bosons behave like “springs” that push the electrons back into \( \mathcal{P}^0 \).

The bosons that stabilize the Cooper pairs are, in any material, the energetically lowest boson excitations of the crystal possessing the crystal spin 1 \( \cdot \) \( \hbar \) and being sufficiently stable to transport it through the crystal. These “crystal-spin-1” bosons are localized excitations \( |\vec{T}, l\rangle \) of well-defined symmetry, which move as Bloch waves through the crystal. Most likely, these \( |\vec{T}, l\rangle \) are coupled phonon-plasmon modes which in the isotropic lattices of the standard superconductors have dominant phonon character. However, in the one- or two-dimensional sublattices of the high-\( T_c \) materials, phonons are not able to carry crystal-spin angular momenta. Here, the \( |\vec{T}, l\rangle \) are energetically higher lying crystal-spin-1 excitations of dominant plasmon character leading within the BCS theory to higher transition temperatures.

I suppose that only quantum mechanical constraining forces as described in this paper are able to produce stable Cooper pairs. This supposition is corroborated by both theoretical arguments and calculated band structures. I have already identified \( \sigma \) bands in the band structures of a great number of superconductors, while I could not find \( \sigma \) bands in the band structures of metals not becoming superconducting. In particular, on the basis of this new mechanism a theoretical interpretation of the Matthias rule was possible in the framework of the BCS theory.

For an examination of calculated band structures in terms of magnetic or superconducting bands the symmetry notations of the Bloch functions in the symmetry points of the Brillouin zone must be known. Unfortunately, these symmetry notations are omitted in nearly all the published band-structure calculations of the new superconductors.
Acknowledgments

I thank Ernst Helmut Brandt for critical comments on the manuscript.

* Electronic address: krueger@mf.mpg.de

1. E. Krüger, Phys. Rev. B 30, 2621 (1984).
2. E. Krüger, J. Supercond. 14(4), 469 (2001).
3. W. Heisenberg, Z. Phys. 49, 619 (1928).
4. E. Krüger, Phys. Rev. B 63, 144403 (2001).
5. N. F. Mott, Can. J. Phys. 34, 1356 (1956).
6. J. Hubbard, Proc. R. Soc. London, Ser. A 276, 238 (1963).
7. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
8. E. Krüger, J. Supercond. 15(2), 105 (2002).
9. E. Krüger, J. Supercond. 14(4), 551 (2001).
10. E. Krüger, Phys. Rev. B 59, 13795 (1999).
11. E. Krüger, phys. stat. sol. b 156, 345 (1989).
12. E. Krüger, phys. stat. sol. b 85, 493 (1978).