Stability of the superconducting state in YBa$_2$Cu$_3$O$_7$

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The nonadiabatic Heisenberg model (NHM) proposed as an extension of the Heisenberg model makes a contribution to the eigenstate problem of superconductivity. The Hamiltonian $H^n$ derived within this group-theoretical model has superconducting eigenstates if and only if the considered material possesses a narrow, roughly half-filled “superconducting” energy band of special symmetry in its band structure. This paper shows that the high-temperature superconductor YBa$_2$Cu$_3$O$_7$ possesses such a superconducting band. This new result together with previous observations about other superconductors and non-superconductors corroborates the theoretical evidence within the NHM that stable superconducting states are connected with superconducting bands. It is proposed that the type of superconductivity, i.e., whether the material is a conventional low-$T_c$ or a high-$T_c$ superconductor, is determined by the energetically lowest boson excitations that carry the crystal spin $1 \cdot \hbar$ and are sufficiently stable to transport this crystal spin-angular momentum through the crystal. This mechanism provides the electron-phonon mechanism that enters the BCS theory in conventional superconductors.

Keywords: superconductivity, nonadiabatic Heisenberg model, group theory

1. INTRODUCTION

To date, it is not possible to solve the Schrödinger equation

$$H\psi = E\psi$$  \hspace{1cm} (1.1)

for superconducting or non-superconducting materials. Hence, the traditional theory of both conventional low-$T_c$ and high-$T_c$ superconductivity has to postulate the existence of superconducting eigenstates $\psi$. The results of the traditional theory have a physical meaning only if superconducting eigenstates exist for the considered material.

In former papers [1, 2] the author proposed an extension of the Heisenberg model of magnetism [3], called nonadiabatic Heisenberg model (NHM). This group-theoretical model goes beyond the adiabatic approximation and gives a contribution to the eigenstate problems of both magnetism and superconductivity. Within the NHM, superconducting eigenstates are connected with the existence of a narrow, roughly half-filled “superconducting band” in the band structure of the considered material. In such a superconducting band the related nonadiabatic Hamiltonian $H^n$ derived within the NHM undoubtedly has superconducting eigenstates because $H^n$ acts in a special part of the Hilbert space which may be called “Cooper space” [4]. This space represents a nonadiabatic system in which constraining forces are effective in a way familiar from the classical mechanics. Below a transition temperature $T_c$, these constraining forces reduce the degrees of freedom of the electron system by forcing the electrons to form pairs that are invariant under time inversion, i.e., by forcing the electrons to form Cooper pairs that possess only half the degrees of freedom of unpaired electrons. Since this pair formation is mediated by boson excitations, the traditional theory of superconductivity provides within the Cooper space the quantitative methods to calculate $T_c$ and other parameters of the superconducting state.

In materials that do not possess a superconducting band, on the other hand, constraining forces that halve the degrees of freedom of the electrons do not exist. In the classical mechanics, however, any reduction of the degrees of freedom of any system of particles is caused by constraining forces. Hence, it cannot be excluded that also in quantum mechanical systems any reduction of the electronic degrees of freedom is produced by constraining forces since quantum particles behave in some respects similar to classical particles. This comparison of the quantum system with a classical system suggests that the constraining forces established within the NHM in superconducting bands are required for the formation of Cooper pairs, i.e., they are required for the Hamiltonian $H$ to possess superconducting eigenstates. Consequently, there is evidence that materials which do not possess a narrow, roughly half-filled superconducting band, do not become superconducting even if the traditional theory of superconductivity predicts a stable superconducting state.

Superconducting bands have already been identified in the band structures of a large number of elemental superconductors [5] and of the high-temperature superconductor La$_2$CuO$_4$ [6]. The theoretical evidence that superconducting bands are required for superconducting eigenstates to exist is corroborated by the fact that superconducting bands cannot be found in those elemental metals (such as Li, Na, K, Rb, Cs, Ca, Cu, Ag, and Au) which do not become superconducting [6]. An investigation into the band structures of the transition metals in terms of superconducting bands straightforwardly leads to the Matthias rule [7].

The aim of the present paper is to investigate whether or not the superconducting state of the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ found by C. W. Chu, M. K. Wu, and co-workers [8] is also connected with the existence of a superconducting band. Before in Sec. [5] the existence
of this band shall be established, in the following Sec. 2 the NHM is shortly described, in Sec. 3 it is shown that the antiferromagnetic structure existing in YBa$_2$Cu$_3$O$_6$ is not stable in YBa$_2$Cu$_3$O$_7$, and Sec. 4 gives the definition of superconducting bands and a short characterization of the mechanism of Cooper pair formation in these bands.

2. NONADIABATIC HEISENBERG MODEL

In the framework of the NHM, the electrons in narrow, roughly half-filled bands may lower their Coulomb energy by occupying an atomiclike state as proposed by Mott [8] and Hubbard [10]: as long as possible the electrons occupy localized states and perform their band motion by hopping from one atom to another. The localized states are represented by localized functions depending on an additional coordinate $\vec{q}$ related to the nonadiabatic motion of the center of mass of the localized state. The introduction of this new coordinate allows a consistent specification of the atomiclike motion that has a lower energy than a purely bandlike motion. The nonadiabatic localized functions must be adapted to the symmetry of the crystal so that the nonadiabatic Hamiltonian $H^n$ has the correct commutation properties.

The nonadiabatic localized functions may be approximated by the best localized (spin-dependent) Wannier functions when the nonadiabatic motion of the centers of mass again is disregarded. These “adiabatic” and our nonadiabatic functions will not differ so strongly that their symmetry is altered at the transition from the adiabatic to the nonadiabatic system. Hence, suitable nonadiabatic localized states allowing an atomiclike motion of the electrons exist if and only if best localized Wannier functions exist which are adapted to the symmetry of the crystal.

3. INSTABILITY OF THE MAGNETIC ORDERED STATE IN YBa$_2$Cu$_3$O$_7$

The antiferromagnetic structure in YBa$_2$Cu$_3$O$_6$ as well as the additional O atom in YBa$_2$Cu$_3$O$_7$ leads to an orthorhombic distortion of the paramagnetic tetragonal crystal. Hence, one could believe that the additional O atom stabilizes the magnetic structure observed in YBa$_2$Cu$_3$O$_6$. However, this is not true because the orthorhombic distortions are basically different. While the magnetic phase in YBa$_2$Cu$_3$O$_6$ has the orthorhombic primitive Bravais lattice $\Gamma_o$, the corresponding magnetic structure in YBa$_2$Cu$_3$O$_7$ would possess the orthorhombic base-centered lattice $\Gamma_{bo}$, see Fig. 1. In YBa$_2$Cu$_3$O$_7$ the magnetic group would have the form

$$ M = H + \{K \mid 1\over 2 \mid 0\} H, $$

where $K$ stands for the operator of time inversion and $H$ denotes a space group with the Bravais lattice $\Gamma_{bo}$.

Within the NHM, both a magnetic state $|m\rangle$ and the time-inverted state

$$ \bar{|m\rangle} = K|m\rangle $$

are eigenstates of a Hamiltonian commuting with the operator $K$ of time inversion. Hence, a stable magnetic state $|m\rangle$ complies with two conditions:
\(|m\) is basis function of a one-dimensional corepresentation of \(M\); 

\(|m\) and the time-inverted state \(|\bar{m}\rangle\) are basis functions of a two-dimensional irreducible corepresentation of the gray magnetic group

\[
\mathcal{M} = M + KM,
\]

see Sec. III.C of Ref. [11].

As in the foregoing paper [12] we have to look for space groups \(H\) possessing at least one one-dimensional single-valued representation \(R\) following

(i) case (a) with respect to the magnetic group \(H + \{K\frac{1}{2},0\}\) and

(ii) case (c) with respect to the magnetic group \(H + KH\).

The cases (a) and (c) are defined in Eqs. (7.3.45) and (7.3.47), respectively, in the textbook of Bradley and Cracknell [13]. The irreducible corepresentation derived from \(R\) stays one-dimensional in case (a) and becomes two-dimensional in case (c).

Among all the space groups with the Bravais lattice \(\Gamma_b\) there are only the two groups \(H_1 = \Gamma_bC_{2h}^3\) (36) and \(H_2 = \Gamma_bC_{2h}^3\) (37) possessing one-dimensional representations following case (c) with respect to \(H_i + KHi_i\) \((i = 1, 2)\).

(The number in parentheses is the international number of the space group.) That means, only these space groups have non-real one-dimensional representations, see Table 5.7 of Ref. [12]. However, applying Eq. 7.3.51 of Ref. [13] to the non-real representations of \(H_1\) or \(H_2\), it turns out that all of them also follow case (c) with respect to \(H_i + \{K\frac{1}{2},0\}\) \((i = 1, 2)\).

Hence, a magnetic structure with the Bravais lattice \(\Gamma_b\) and with the anti-unitary operation \(\{K\frac{1}{2},0\}\) is not stable in \(\text{YBa}_2\text{Cu}_3\text{O}_6\). This material does not possess a magnetic structure corresponding to the magnetic structure in \(\text{YBa}_2\text{Cu}_3\text{O}_7\). However, it cannot be excluded that other, more complex magnetic structures might be stable in \(\text{YBa}_2\text{Cu}_3\text{O}_7\).

4. SUPERCONDUCTING BANDS

In \(\text{YBa}_2\text{Cu}_3\text{O}_6\) the Bloch functions of the half-filled “antiferromagnetic band” can be unitarily transformed into best localized Wannier functions situated on the Cu sites and adapted to the symmetry of the magnetic structure existing in this material. Hence, the electrons may lower their Coulomb energy by occupying an atomiclike state represented by these Wannier functions [12]. In \(\text{YBa}_2\text{Cu}_3\text{O}_7\), on the other hand, the electrons cannot lower their Coulomb energy in the same way because the magnetic structure existing in \(\text{YBa}_2\text{Cu}_3\text{O}_6\) is not stable in \(\text{YBa}_2\text{Cu}_3\text{O}_7\).

In \(\text{YBa}_2\text{Cu}_3\text{O}_7\) the electrons have another way to occupy the energetically favorable atomiclike state. As I shall show in the following Sec. 5 this material possesses a narrow, roughly half-filled “superconducting band” [1, 2, 4] in its band structure, see Fig. 2. An energy band of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) is called “superconducting band” when the Bloch functions of this band can be unitarily transformed into spin-dependent Wannier functions which are

- centered on the Cu sites;
- symmetry-adapted to the space group \(H = \Gamma_oD_{2h}^1\) of this material; and
- best localized.

In this context I assume the localized states to have the same positions as they have in the antiferromagnetic state of \(\text{YBa}_2\text{Cu}_3\text{O}_6\) [12]. A superconducting band in \(\text{YBa}_2\text{Cu}_3\text{O}_7\) consists of three branches because there are three Cu atoms in the unit cell. Since \(\text{YBa}_2\text{Cu}_3\text{O}_7\) possesses a narrow, roughly half-filled superconducting band, the electrons in this material may lower their Coulomb energy by occupying an atomiclike state represented by spin-dependent Wannier functions.

Within the adiabatic approximation, an atomiclike motion with localized functions depending on the electron spin does not conserve the spin angular momentum. In the (real) nonadiabatic system, however, the electrons may interchange spin angular momenta with the lattice of the atomic cores. In the framework of the NHM, an atomiclike motion with localized functions depending on the electron spin leads to a special spin-boson interaction in the nonadiabatic system: at any electronic scattering process two crystal-spin-1 bosons are excited or absorbed.

At low temperature, this spin-boson interaction has a striking feature distinguishing it from any usual electronphonon or electron-boson interaction: it constrains the electrons in a special way to form electron pairs invariant under time inversion because the conservation of spin angular momentum would be violated in any unpaired state. This mechanism of pair formation shows resemblances, but also an important difference when compared with the familiar mechanism of Cooper pair formation presented within the Bardeen-Cooper-Schrieffer (BCS) theory [17]. The difference between both mechanisms can be described in terms of constraining forces that halve the degrees of freedom of the electrons [4], or in terms of “spring-mounted” Cooper pairs [15].

Electron pairs invariant under time inversion cause superconductivity. The superconducting transition temperature may be approximately calculated by the familiar BCS formula

\[
T_c = 1.14 \cdot \theta \cdot e^{-1/N(E_F)V}
\]

where now \(N(E_F)\), \(V\) and \(\theta\) are the density of states of the electrons of the superconducting band at the Fermi
level, the effective spin-phonon interaction, and the Debye temperature, respectively. The Debye temperature $\theta$ now is related to the spectrum of the energetically lowest excitations of the crystal possessing the crystal spin $1 \cdot \hbar$ and being sufficiently stable to transport it through the crystal, see also Sec. 6.

5. SUPERCONDUCTING BAND IN YBa$_2$Cu$_3$O$_7$

In this section I show that the energy band denoted in Fig. 2 by the bold line is a superconducting band with weakly spin-dependent Wannier functions. It is labeled by the representations

$$\Gamma_4^+, \Gamma_2^+, \Gamma_2^-, \Gamma_2^+;$$
$$X_1^+, X_1^+, X_1^+;$$
$$S_3^+, S_3^+, S_3^+;$$
$$Y_3^+, Y_3^+, Y_3^+;$$
$$Z_3^+, Z_3^+, Z_3^+, Z_3^+;$$
$$U_3^+, U_3^+, U_3^+;$$
$$R_3^+, R_3^+, R_3^+;$$
$$T_3^+, T_3^+, T_3^+.$$  (5.5)

Table II (a) lists all the (eight) bands in YBa$_2$Cu$_3$O$_7$ whose Bloch functions can be unitarily transformed into symmetry-adapted and best localized Wannier functions situated on the Cu sites. Each band consists of three branches because there are three Cu atoms in the unit cell. While the representations (5.5) coincide with the representations of band 1 in Table II (a) at points $X, S, Y, U, R,$ and $T$, the representations at points $\Gamma$ and $Z$ are slightly different: band 1 in Table II (a) contains $\Gamma_4^+$ as well as $Z_3^+$ twice, but these representations are found only once among the representations (5.5). Hence, we cannot represent the Bloch functions of this band by symmetry-adapted and best localized Wannier functions situated on the Cu sites.

The situation is changed when we replace the single-valued representations $R^\pm_i$ by the corresponding double-valued representations $R^\pm_i \times D_{1/2}$. From Table II (b) we can derive that

$$R^\pm_i \times D_{1/2} = R^\pm_5$$  (5.6)

holds for any representation $R^\pm_i$ in Table II (a). $D_{1/2}$ denotes the two-dimensional double-valued representation of the three-dimensional rotation group $O(3)$ given, e.g., in Table 6.1 of Ref. [13]. Table II (b) lists all
the superconducting bands in YBa$_2$Cu$_3$O$_7$. The energy band characterized by the representations $5.5$ now becomes identical with band 1 in Table II (b). The Bloch functions of the band $5.5$ can be unitarily transformed into symmetry-adapted and best localized spin-independent Wannier functions situated on the Cu sites. At points $\Gamma$ and $Z$ we may use the Bloch functions with the underlined representations $5.5$.

The Wannier functions are weakly spin-dependent since they do not strongly differ from the spin-independent Wannier function belonging to band 1 in Table II (a). It is only one of the two representations $2\Gamma_1^+$ and $2Z_1^+$, respectively, of band 1 in Table II (a) which does not belong to the superconducting band $5.5$.

6. DISCUSSION

This paper shows that the high-temperature superconductor YBa$_2$Cu$_3$O$_7$ possesses a narrow, roughly half-filled “superconducting band” in its band structure, see Fig. 2 which enables the electrons to occupy the energetically favorable atomiclike state represented by spin-independent Wannier functions. Within the NHM, the spin-dependence of the localized functions has an important consequence: at zero temperature, the electrons must form pairs invariant under time inversion because the conservation of spin angular momentum would be

| Table I: Character tables of the irreducible representations $R^2_i$ of the space group $Pmmn = \Gamma_oD_{2h}^5$ (47) of YBa$_2$Cu$_3$O$_7$. |
|-------------------------------------------------|
| (a) Single-valued representations |
| $E$ $C_{2z}$ $C_{2y}$ $C_{2x}$ $I$ $\sigma_z$ $\sigma_y$ $\sigma_x$ |
| $R^1_i$ 1 1 1 1 1 1 1 |
| $R^2_i$ 1 -1 1 -1 1 -1 1 |
| $R^1_2$ 1 1 -1 -1 1 1 -1 |
| $R^2_2$ 1 -1 1 1 -1 1 -1 |
| $R^1_3$ 1 1 1 -1 1 -1 1 |
| $R^2_3$ 1 -1 1 -1 1 1 -1 |
| $R^1_4$ 1 -1 -1 -1 1 1 1 |
| $R^2_4$ 1 1 -1 1 -1 1 1 |

(b) Double-valued representations

| $E$ $\bar{C}_{2z}$ $\bar{C}_{2y}$ $\bar{C}_{2x}$ $I$ $\bar{\sigma}_z$ $\bar{\sigma}_y$ $\bar{\sigma}_x$ |
|-------------------------------------------------|
| $R^1_5$ 2 -2 0 0 0 0 0 |
| $R^2_5$ 2 -2 0 0 -2 0 0 |

Notes to Table I

(i) The two tables (a) and (b) are common to all the points of symmetry $\Gamma(000)$, $Y(\frac{1}{4}0\frac{1}{4})$, $S(\frac{1}{4}\frac{1}{4}0)$, $X(0\frac{1}{4}0)$, $Z(00\frac{1}{4})$, $T(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $R(\frac{1}{4}0\frac{1}{4})$, and $U(0\frac{1}{4}\frac{1}{4})$ in the Brillouin zone for $\Gamma_o$.

(ii) The letter $R$ has to be replaced by the letter denoting the relevant point of symmetry.

(iii) The tables are determined from Tables 5.7 and 6.13 in the textbook of Bradley and Cracknell [13].

| Table II: Single- and double-valued representations of all the energy bands in YBa$_2$Cu$_3$O$_7$ with symmetry-adapted and optimally localized (spin-dependent) Wannier functions centered at the Cu atoms. |
|-------------------------------------------------|
| (a) Single-valued representations |
| Band 1 2$R^1_i + R^5_i$ |
| Band 2 2$R^1_i + R^5_i$ |
| Band 3 2$R^1_i + R^5_i$ |
| Band 4 2$R^1_i + R^5_i$ |
| Band 5 2$R^1_i + R^5_i$ |
| Band 6 2$R^1_i + R^5_i$ |
| Band 7 2$R^1_i + R^5_i$ |
| Band 8 2$R^1_i + R^5_i$ |

Notes to Table II

(i) The two tables (a) and (b) are common to all the points of symmetry $\Gamma$, $Y$, $S$, $X$, $Z$, $T$, $R$, and $U$ in the Brillouin zone for $\Gamma_o$.

(ii) The letter $R$ has to be replaced by the letter denoting the relevant point of symmetry.

(iii) The two bands with the double-valued representations (b) form superconducting bands.

(iv) The representations can be identified from Table I.

(v) Each row defines one band consisting of three branches, because there are three Cu atoms in the unit cell.

(vi) The bands are determined by Eq. (B7) of Ref. [6].

(vii) Assume a band of the symmetry in any row of this table to exist in the band structure of a given material with the space group $\Gamma_oD_{2h}^5$. Then the Bloch functions of this band can be unitarily transformed into Wannier functions that are

- as well localized as possible;
- centered at the Cu atoms; and
- symmetry-adapted to the space group $\Gamma_oD_{2h}^5$.

These Wannier functions are usual (spin-independent) Wannier function if the considered band is characterized by the single-valued representations (a). They are spin-dependent if the band is characterized by the double-valued representations (b).
violated in any unpaired state. Hence, at zero temperature, the atomiclike state in a superconducting band is superconducting of necessity. The related nonadiabatic Hamiltonian $H^n$ clearly has superconducting eigenstates.

This result suggests that the superconducting state in YBa$_2$Cu$_3$O$_7$ is stabilized by the constraining forces that are effective in narrow superconducting bands. Both magnetism and superconductivity have the same physical origin: they exist because the electrons at the Fermi level tend to occupy the energetically favorable atomiclike state. The special symmetry properties of the related Wannier function determine whether the material becomes magnetic or superconducting (or has a property not yet considered). From this angle, superconductivity might also be called “$k$-space magnetism”.

The superconducting transition temperature is approximately determined by the BCS equation (4.4) with the Debye temperature $\theta$ being related to the spectrum of the energetically lowest boson excitations of the crystal that possess the crystal spin $\mathbf{T} \cdot \mathbf{h}$ and are sufficiently stable to transport it through the crystal. These “crystal-spin-$\mathbf{1}$” bosons are localized excitations $|\mathbf{T}, l\rangle$ (with $l = -1, 0, +1$ labeling the three directions of the crystal spin and $\mathbf{T}$ denoting a lattice point) of well-defined symmetry $1 \parallel 18$ which propagate as Bloch waves (with the crystal momentum $\hbar \mathbf{k}$) through the crystal.

The $|\mathbf{T}, l\rangle$ are generated during spin-flip processes in the superconducting band and must carry off the surplus spin angular momenta generated at these processes. This spin-phonon mechanism suggests that the $|\mathbf{T}, l\rangle$ are coupled modes of lattice vibrations and vibrations of the core electrons against the atomic lattice: In a first step the atomiclike electrons in the superconducting band transmit their angular momenta to the core electrons by generating a plasmon-like vibration of the core electrons against the atoms. In a second step, these plasmon-like excitations generate phonon-like vibrations of lower energy if phonons of the appropriate symmetry are sufficiently stable.

Thus, it is proposed that the $|\mathbf{T}, l\rangle$ are coupled phonon-plasmon modes which determine the type of superconductivity. They have dominant phonon character in the isotropic lattices of the transition elements and, hence, confirm the electron-phonon mechanism that enters the BCS theory in these materials. However, phonon-like excitations are not able to transport crystal-spin angular-momenta within the two-dimensional copper-oxygen layers of YBa$_2$Cu$_3$O$_7$, see, for preliminary ideas to this problem, Ref. 15. Within the two-dimensional layers, the $|\mathbf{T}, l\rangle$ necessarily are energetically higher lying excitations of dominant plasmon character leading in the BCS equation (4.3) to a higher Debye temperature $\theta$ and, hence, to a higher $T_c$. This interpretation is corroborated by the experimental evidence for two-dimensional superconductivity in the CuO$_2$ atomic plains 19, 20, 21, 22, 23.

In the band structures of the high-temperature superconductors YBa$_2$Cu$_3$O$_7$ (this paper) and La$_2$CuO$_4$ 6 I discovered an absolutely new feature of the superconducting bands: the related Wannier functions are weakly spin-dependent. I believe that this weak spin-dependence is an additional condition for stable two-dimensional high-$T_c$ superconducting states. This question requires further theoretical considerations and further examinations of the band structures of high-$T_c$ superconductors.

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