The reason why doping causes superconductivity in LaFeAsO

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(Dated: November 7, 2018)

The experimental observation of superconductivity in LaFeAsO appearing on doping is analyzed with the group-theoretical approach that evidently led in a foregoing paper (J. Supercond 24:2103, 2011) to an understanding of the cause of both the antiferromagnetic state and the accompanying structural distortion in this material. Doping, like the structural distortions, means also a reduction of the symmetry of the pure perfect crystal. In the present paper we show that this reduction modifies the correlated motion of the electrons in a special narrow half-filled band of LaFeAsO in such a way that these electrons produce a stable superconducting state.

Keywords: superconductivity, nonadiabatic Heisenberg model, group theory

I. INTRODUCTION

Undoped LaFeAsO does not become superconducting at any temperature but rather undergoes a structural distortion from tetragonal to orthorhombic symmetry at \( \sim 155 \text{K} \) as well as an antiferromagnetic spin ordering transition at \( \sim 137 \text{K} \) \cite{1,2}. As oxygen is gradually replaced with fluorine, however, the antiferromagnetic order in the doped material LaFeAsO\(_{1-x}F_x\) disappears and a superconducting state occurs at the relatively small doping level \( x \approx 0.05 \). When \( x \) continues to increase the orthorhombic structural distortion coexists with superconductivity until the superconducting phase becomes tetragonal at doping levels \( x \geq 0.08 \) \cite{3,4}. On the other hand, there is no experimental evidence of the antiferromagnetic order coexisting with the superconducting state.

The evidently successful foundation of the existence of both the antiferromagnetic state and the accompanying structural distortion in LaFeAsO given in a foregoing paper \cite{5} has led us to consider now the superconducting state and the orthorhombic non-magnetic distortion of LaFeAsO using the same approach. Though this approach is unusual in the superconductivity field, it corroborates the generally accepted idea that correlated electrons are responsible for the superconducting state. It is based on a group theoretical treatment of correlated atomic-like electrons (Sec. II.1) in narrow, half-filled “superconducting bands” of special symmetry as they are considered within a nonadiabatic extension of the Heisenberg model, the nonadiabatic Heisenberg model (NHM). We will put also emphasis on making clear the underlying physical ideas of this model.

In Sec. II we sketch the central role of superconducting bands (as they shall be defined in the Appendix A) in Cooper pair formation within the NHM. Then, in Sec. III we show that tetragonal undoped LaFeAsO (with the space group \( P4/nmm \) \cite{1,9,10}) does not possess a superconducting band. However, a superconducting band does appear in the band structure of LaFeAsO when the symmetry of the material is reduced. As is shown, this reduction can be realized by the doping (Sec. IV) or by an orthorhombic distortion of the crystal (Sec. V).

II. SUPERCONDUCTING BANDS AND SUPERCONDUCTIVITY

In this section we outline the mechanism of Cooper pair formation within the NHM, for more detailed summaries see Ref. \cite{14} or \cite{15}.

II.1. Nonadiabatic Heisenberg model

The NHM was defined in Ref. \cite{8}. It is based on three postulates concerning the atomic-like motion of the electrons in narrow, half-filled energy bands as it was first considered by Mott \cite{16} and Hubbard \cite{17}: the electrons occupy localized states as long as possible and perform their band motion by hopping from one atom to another. The three postulates of the NHM are physically evident, emphasize the correlated nature of any atomic-like motion, and require the introduction of nonadiabatic localized states. In this way the NHM refines the original treatment of atomic-like electrons as it was given by Mott and Hubbard. Fortunately, only the symmetry of the localized functions representing the nonadiabatic localized states need to be known. Within the NHM they have the same symmetry and spin dependence as the best localized exact Wannier functions of the considered partly filled energy band. In this context, “exact” Wannier functions form a complete basis of the Bloch functions that really exist in the band.

An important feature of the NHM is the existence of the nonadiabatic condensation energy \( \Delta E \) as defined in Eq. (2.20) of Ref. \cite{8}: the electron system gains \( \Delta E \) at the transition from a purely bandlike state to the correlated (nonadiabatic) atomic-like state. This energy gain is caused by the Coulomb correlation energy and, thus, the NHM yields an important and novel contribution to the theory of correlated electrons.
II.2. New mechanism of Cooper pair formation

In case the considered energy band is a superconducting band, the related Wannier functions are spin-dependent, see the detailed definition given in the Appendix [A]. The symmetry of these Wannier functions ensures that the nonadiabatic Hamiltonian $H^a$ commutes correctly with the symmetry operations of the space group. Their spin dependence, on the other hand, has the far reaching consequence that only in special atomic-like states the electrons satisfy the conservation of spin angular-momentum. For this reason the Coulomb interaction in a narrow, roughly half-filled superconducting band produces an interaction between the electron spins and “crystal-spin-1 bosons”. These crystal-spin-1 bosons are the energetically lowest boson excitations of the crystal that possess the crystal-spin angular momentum $1 \cdot \hbar$ and are sufficiently stable to transport it through the crystal.

Below a certain transition temperature $T_c$, this spin-boson interaction forces the electrons in a novel way to form Cooper pairs. On the one hand, the crystal-spin-1 bosons mediate the formation of Cooper pairs as it is already described in the classical [21] theory of superconductivity. In addition, however, the crystal-spin-1 bosons in a narrow superconducting band produce constraining forces as they are familiar from classical mechanics: below $T_c$ they 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. A comparison of the quantum system with a classical system suggests that these constraining forces operating in a narrow, roughly half-filled superconducting band are required for the Hamiltonian of the system to possess eigenstates in which the electrons form Cooper pairs. Thus, the fundamental contribution of the NHM to the theory of superconductivity is the assertion that only crystal-spin-1 bosons in a narrow superconducting band are able to produce Cooper pairs. The NHM predicts that a material can become superconducting only if this material has a narrow, roughly half-filled superconducting band in its band structure. This fundamental statement of the NHM is already corroborated by numerous superconductors and non-superconductors, see Sec. [VII].

Constraining forces do not alter the energy of the electron system but only lower the degrees of freedom. Thus, the vast majority of the statements and calculations of the traditional theory of superconductivity should stay valid in a superconducting band.

III. SUPERCONDUCTIVITY FORBIDDEN IN PURE PERFECT LaFeAsO

Consider the energy band denoted in Fig. [1]by the bold lines which in the following shall be called the “active band” of LaFeAsO. In this section we show that neither this active band nor any other roughly half-filled energy band of perfect LaFeAsO is a superconducting band.

First, consider spin-dependent Wannier functions that are situated on the Fe sites. Table [B.1] (b) lists the double-valued representations of all the superconducting bands in tetragonal undoped LaFeAsO with the spin-dependent Wannier functions situated on the Fe sites. Each of these two superconducting bands consists of two branches because there are two Fe atoms in the unit cell. Table [B.1] (b) shows that the two branches of either superconducting band are degenerate at the points $M$ and $A$ because, in each of these points, the Bloch functions belong only to one (double-valued) representation, namely to the four-dimensional representation $M_5$ and $A_5$, respectively.

The two branches of the active band of LaFeAsO, on the other hand, are split at points $M$ and $A$. Thus, it is not identical with one of the superconducting bands listed in Table [B.1] (b). Even if we allow the related spin-dependent Wannier functions to be centered at the La, As, or O atoms, the active band does not become a superconducting band because the two branches of any superconducting band in tetragonal undoped LaFeAsO are degenerate at points $M$ and $A$. This important feature follows from the mere fact that both points $M$ and $A$ possess in the space group $P4/nnm$ only one double-valued representation, namely the four-dimensional representation $M_5$ and $A_5$, respectively, see Table 6.13 of Ref. [21].

Consequently, the active band is not a superconducting band. We can neither combine the bands near the Fermi level in the band structure of LaFeAsO in any other way to form a continuous superconducting band. Any roughly half-filled energy band in tetragonal undoped LaFeAsO (consisting of two branches) which is compatible with either superconducting band in Table [B.1] (b) would have a considerable gap between $M$ and $X$ and between $A$ and $R$, which extends over the whole plane $MXR$. Such a strongly discontinuous energy band, however, does not yield best localized spin-dependent Wannier functions and, hence, is unsuitable to represent atomic-like electrons.

To sum up, in the band structure of perfect LaFeAsO a superconducting band does not exist, and thus superconductivity cannot develop.

IV. SUPERCONDUCTIVITY IN WEAKLY DOPED LaFeAsO

IV.1. The space group $P\overline{4}mm2$ of weakly doped LaFeAsO

The doped material LaFeAsO$_{1-x}$F$_x$ (with $x > 0$) no longer possesses any space group symmetry because the doping destroys the translation symmetry of the crystal. Thus, the electrons no longer move in a potential invariant under the tetragonal space group $P4/nnm$. How-
ever, even in the doped material the array of the Fe atoms is invariant under the translations of $P4/nmm$. Therefore we describe approximately for small doping levels $x$ the atomic-like state related to the Fe atoms by an idealized atomic-like state in a potential which still is invariant under a tetragonal space group $S$. The best choice of this space group $S$ is that subgroup of $P4/nmm$ which is best adapted to the local symmetry of the oxygen-fluorine layers. Thus, we get the optimal choice of the group $S$ by removing from $P4/nmm$ all the (proper and improper) rotations and reflections not leaving invariant the positions of the fluorine atoms. In this way we obtain the group $S = P\overline{4}m2 = \Gamma_q D_5^{2d}$ (115) still possessing the tetragonal-primitive Bravais lattice $\Gamma_q$.

Hence, we use the group $P\overline{4}m2$ as the space group of the atomic-like electrons centered on the Fe sites in weakly doped LaFeAsO. This group can be defined by the two generating elements

$$\{S_{1z}\} = \{0, \frac{1}{2}, 0\}, \text{ and } \{|C_{2a} T_{1z}\},$$

(1)
cf. Table 3.7 of Ref. [21] and Table I. The symmetry operations (1) are given in the coordinate system defined in Fig. 2 (a). The generating elements define a group because every element of the group is expressible as a product of powers of the generating elements. Hence, a given structure is invariant under all the symmetry operations of a space group if it is invariant under the generating elements.

### IV.2. Superconducting band in the space group $P\overline{4}m2$

In this section we show that the active band of LaFeAsO becomes a superconducting band in the space group $P\overline{4}m2$ of doped LaFeAsO. For this purpose we unitarily transform the Bloch functions of the active band into Bloch functions adapted to the symmetry of the space group $P\overline{4}m2$, while the run of the active band in the band structure of LaFeAsO is assumed to be not considerably affected by the doping.

Table B.6 lists all the energy bands in LaFeAsO whose Bloch functions can be unitarily transformed into best localized Wannier functions [Table B.6 (a)] or spin-dependent Wannier functions [Table B.6 (b)] which are centered at the Fe atoms and are symmetry-adapted to the space group $P\overline{4}m2$.

Comparing the bands listed in Table B.6 with the bands given in Table B.5, we see the important difference between these bands: while the two branches...
FIG. 2. Coordinate systems and unit cells of tetragonal (a) and orthorhombically distorted (b) non-magnetic LaFeAsO. For reasons of clarity, only the iron and oxygen atoms are shown, where one of the two oxygen atoms in (a) is replaced by fluorine. \(a, b,\) and \(c\) denote the lengths of the sides in the unit cells. The coordinate systems define the symmetry operations \(\{R|pqr\}\) as used in this paper. They are written in the Seitz notation as detailed in the textbook of Bradley and Cracknell [21]: \(R\) stands for a point group operation and \(pqr\) denotes the subsequent translation. The point group operation \(R\) is related to the \(x, y, z\) coordinate system and \(pqr\) stands for the translation \(t = pT_1 + qT_2 + rT_3\). As defined in Table 3.1 of Ref. [21], the basic translations \(T_i\) have different directions in the tetragonal and orthorhombic structure. The depicted displacements of the Fe and O atoms in (b) realize the orthorhombic space group \(P\ mm_2\ (25)\) which allows the onset of superconductivity, see Sec. IV. The Fe and O atoms are displaced in \(\pm z\) direction where the amount of the displacements of the Fe atoms or of the O atoms in the unit cell is different in order to distinguish \(P\ mm_2\) from the space group \(P\ mmn\ (59)\).

According to Table B.1 we may unitarily transform these functions into Bloch functions labeled by the representations

\[
\begin{align*}
\Gamma_2^- & \rightarrow \Gamma_4, & \Gamma_3^+ & \rightarrow \Gamma_3; \\
M_3 & \rightarrow M_5, & M_4 & \rightarrow M_2 + M_4; \\
A_3 & \rightarrow A_5, & A_2 & \rightarrow A_1 + A_3; \\
Z_1^+ & \rightarrow \overline{Z}_1, & Z_4^- & \rightarrow \overline{Z}_1; \\
R_1 & \rightarrow R_1 + R_4, & R_3 & \rightarrow R_1 + R_4; \\
X_1 & \rightarrow \overline{X}_1 + X_4, & X_1 & \rightarrow X_1 + X_4.
\end{align*}
\]

The underlined representations belong to a band listed in Table B.6 namely to band 4 in Table B.6 (a). The two representations \(M_5\) and \(A_5\), however, are not part of band 4. Thus, we cannot unitarily transform the Bloch functions of the active band into usual (i.e., spin-independent) Wannier functions being best localized, centered at the Fe atoms, and symmetry-adapted to the group \(P\ mm2\). [The single-valued representations \(M_5\) and \(A_5\) of \(P\ mm2\) listed in (3) should not be confused with the Brillouin zone \(\Gamma_q\).]
TABLE 1. Space groups of LaFeAsO as determined in this paper and in Ref. [7].

| Inter- | Schönhflies | Inter- | Coordinate | t_{bc} | t_{int} | Description | Doping |
| nat. | sym | nat. | system and | | | | |
| symbol | number | | displace- | | | | |
|ments of Fe and O | | | | | | | |

| Imma | \Gamma_v D_{2h}^{25} | 74 | Fig. 3 (b) | \frac{1}{2}T_3 + \frac{1}{2}T_2 + \frac{1}{2}T_3 | Hypothetical antiferromagnetic structure in undistorted LaFeAsO | undoped |
| Pmm2 | \Gamma_0 C_{2v}^{10} | 34 | Fig. 3 (c) | \frac{1}{2}T_2 - \frac{1}{2}T_1 + \frac{1}{2}T_2 | Antiferromagnetic structure in distorted LaFeAsO | undoped |
| P\bar{4}m2 | \Gamma_4 D_{2d}^{11} | 115 | Fig. 2 (a) | \frac{1}{2}T_2 - \frac{1}{2}T_1 - \frac{1}{2}T_2 | Tetragonal LaFeAsO including the weakly doped tetragonal superconducting phase | weakly doped |
| P\bar{4}m2 | \Gamma_0 C_{2v}^{10} | 25 | Fig. 2 (b) | \frac{1}{2}T_1 + \frac{1}{2}T_2 | Non-magnetic orthorhombically distorted LaFeAsO including the weakly doped orthorhombic superconducting phase | weakly doped |

Notes to Table 1

(i) *Imma* is the space group of the experimentally observed antiferromagnetic structure in LaFeAsO as given in Fig. 4 of Ref. [7]. We call it “hypothetical” because it is unstable in undistorted LaFeAsO.

(ii) In any case, the orthorhombic distortion of LaFeAsO is realized by the indicated displacements of the Fe and O atoms alone.

(iii) The origin of the coordinate system used in Ref. [21] and in the *International Tables for Crystallography* is translated into the origin used in this paper by the indicated vectors t_{bc} and t_{int} = t_{bc} + t_0, respectively, where t_0 is given in Table 3.7 of Ref. [21]. Hence, the space group elements P^\prime p used in this paper may be determined by the equations P^\prime p = \{E \mid t_{bc}\} P_{bc} \{E\} - t_{bc} and P^\prime p = \{E \mid t_{int}\} P_{int} \{E\} - t_{int} from the space group elements P_{bc} and P_{int} of Ref. [21] and of the *International Tables*, respectively, where E denotes the indentity operation.

double-valued representations M_5 and A_5 of P4/nmm considered in Sec. [III].

The situation is changed when we allow the Wannier functions to be spin-dependent. In this case we may replace the single-valued representations R_i by the corresponding *double-valued* representations R_i \times D_{1/2}, where 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. [21]. Table [III] lists all the representations R_i \times D_{1/2} in the space group P\bar{4}m2. In particular, it shows that the two unsuitable representations M_5 and A_5 in [III] split at the transition from the single-valued to the double-valued representations,

\begin{align}
M_5 \times D_{1/2} &= M_6 + M_7, \\
A_5 \times D_{1/2} &= A_6 + A_7.
\end{align}

For that reason, the active band becomes identical with band 2 in Table [III] (b). Consequently, the Bloch functions of the active band can be unitarily transformed into *spin-dependent* Wannier functions being best localized, centered at the Fe atoms, and symmetry-adapted to the group P\bar{4}m2. These Wannier functions are only *weakly* spin-dependent because it is only the two representations M_5 and A_5 in [III] which are not part of band 4 in Table [III] (a). This observation together with former observations on La_2CuO_4 [22], YBa_2Cu_3O_7, and MgB_2 [23] suggests that this weak spin dependence is an additional condition for stable high-\texttau superconductivity.

To sum up, within the space group P\bar{4}m2 the active band of LaFeAsO is a superconducting band related to the Fe atoms. Consequently, in the doped material the electron system may gain the nonadiabatic condensation energy \Delta E by producing the special spin-boson interaction acting in a superconducting band. Due to this interaction, the electrons are forced to form Cooper pairs below a certain transition temperature. The resulting superconducting state is experimentally well-established [2].

V. SUPERCONDUCTIVITY IN DISTORTED LaFeAsO

The doping reduces the symmetry of pure LaFeAsO in such a way that the active band of LaFeAsO becomes a superconducting band (preceding Sec. [V]). However, the same effect may have a reduction of the symmetry produced by a spatial distortion of undoped LaFeAsO. There are several subgroups of the space group P4/nmm of tetragonal undoped LaFeAsO allowing a stable super-
conducting state. In view of the experimental results on LaFeAsO, we restrict ourselves to the distortion of the lattice produced by the (small) displacements of the Fe and O atoms depicted in Fig. 2 (b). Depending on whether or not the unit cell of LaFeAsO is doubled in z direction, these displacements realize the orthorhombic space group $Pmm2$ (25) or the tetragonal space group $P4_{2}mc$ (105).

V.1. The orthorhombic space group $Pmm2$ (25) with single unit cell

Removing from the space group $P4/nmm$ all the symmetry operations not leaving invariant the displaced Fe and O atoms as depicted in Fig. 2 (b), we obtain the orthorhombic space group $Pmm2$ defined by the two generating elements

$$\{\sigma_{x}|\frac{1}{2}00\} \text{ and } \{\sigma_{y}|\frac{1}{2}00\},$$

as given in Table 3.7 of Ref. [21], which in this paper are transformed into the coordinate system defined by Fig. 2 (b), see Table II.

A band identified as superconducting band in the space group $P4_2m2$ is a superconducting band in any subgroup of $P4_2m2$, too. To show that within our coordinate systems $Pmm2$ is a subgroup of $P4_2m2$, we write the translations of the generating elements in Eq. (5) in terms of the basic translations of the Bravais lattice $\Gamma_{q}$ of $P4_2m2$ as depicted in Fig. 2 (a). So we get the symmetry operations $\{\sigma_{x}|\frac{1}{2}00\}$ and $\{\sigma_{y}|\frac{1}{2}00\}$, which in fact are elements of $P4_2m2$, see the symmetry operations belonging to point $\Gamma$ in Table I. Hence, the active band of LaFeAsO is a superconducting band in the orthorhombically distorted material with the space group $Pmm2$. Consequently, the displacements of the Fe and O atoms depicted in Fig. 2 (b) enable the electron system to gain the nonadiabatic condensation energy $\Delta E$ by occupying an atomic-like state producing the interaction of the electron spins with crystal-spin-1 bosons leading to superconductivity.

The fact that $Pmm2$ is a subgroup of $P4_2m2$ has another important consequence: the orthorhombic structural distortion with the space group $Pmm2$ is not destroyed by the doping. That means that the superconducting state enabled by the orthorhombic distortion can coexist with the doping, as it is experimentally observed [5].

V.2. The tetragonal space group $P4_{2}mc$ (105) with doubled unit cell

The displacements of the Fe and O atoms as depicted in Fig. 2 (b) realize a further subgroup of $P4/nmm$ if the unit cell of LaFeAsO is doubled in z direction. In this case, the displacements no longer are periodic with $T_{3}$ as given in Fig. 2 (b) but a translation by $T_{3}$ effects an inversion of the displacements as depicted in Fig. 3 (c) of Ref. [7].

These displacements of the Fe and O atoms with doubled unit cell realize the space group $P4_{2}mc$ which would allow a stable superconducting state, too. However, $P4_{2}mc$ is tetragonal which contradicts the experimental observation that the non-magnetic distortion observed in LaFeAsO [1-4] is orthorhombic. In addition, $P4_{2}mc$ is not a subgroup of the space group $P4_2m2$ of the weakly doped material. Consequently, if $P4_{2}mc$ would be realized in LaFeAsO, we could hardly understand the experimental observation [5] that the non-magnetic distortion can survive in the doped system. So we propose that the non-magnetic distortion of LaFeAsO possesses the orthorhombic space group $Pmm2$ rather than the tetragonal space group $P4_{2}mc$.

VI. CONCEPT OF CORRELATED ELECTRONS IN PURE AND DOPED LaFeAsO

In the present and the preceding paper [7] we report evidence that the correlated atomic-like motion of the electrons in magnetic or superconducting bands produces the structural distortion, the antiferromagnetic and the superconducting state in pure or doped LaFeAsO. Our findings shall be summarized in this section and are illustrated in the schematic structural phase diagram shown in Fig. 3.

In Sec. III we have shown that undoped tetragonal LaFeAsO does not possess a superconducting band. The symmetry of the space group $P4/nmm$ produces band degeneracies which make it impossible to construct a superconducting band in the band structure of undoped tetragonal LaFeAsO. Thus, the electron system cannot gain the nonadiabatic condensation energy $\Delta E$ by occupying an atomic-like state producing the spin-boson interaction leading to superconductivity.

However, in Ref. [6] we could show that undoped LaFeAsO possesses a magnetic band related to the experimentally observed antiferromagnetic structure. Thus, the system may lower its correlation energy by occupying an atomic-like state producing the antiferromagnetic order as is experimentally well-established [1-4] below 137K. This magnetic structure is necessarily accompanied by a structural distortion of the crystal with the space group $Pmm2$ going beyond the magnetostriction. This distortion is realized by a displacement of the Fe and O atoms which is also experimentally established [1]. Nevertheless, the electron system in undoped LaFeAsO has another possibility to gain $\Delta E$ in a non-magnetic state: the displacements of the Fe and O atoms depicted in Fig. 2 (b) realize the orthorhombic space group $Pmm2$ possessing a superconducting band and, consequently, allowing an atomic-like state which produces spin-boson interaction. We suppose that this spin-boson interaction is active between 155K and 137K, that is, in the non-magnetic region which is nonetheless orthorhombically distorted. The spin-boson interaction would produce Cooper pairs below a transition temperature $T_{c}$.
TABLE 2. Subgroup diagram of the space groups listed in Table 1

\[
\begin{array}{c}
P4/nmm \\
\downarrow \\
Imma \\
\downarrow \\
P4m2 \\
\downarrow \\
Pmm2 \\
\end{array}
\]

Notes to Table 2

(i) \(P4/nmm\) is the space group of tetragonal paramagnetic \(\text{LaFeAsO}\).

(ii) An arrow points to the subgroup of the group at the tail of the arrow.

(iii) Neither \(Imma\) nor \(Pmm2\) is a subgroup of \(P4m2\). Consequently, the doping destroys the antiferromagnetic order.

(iv) \(Pmm2\) is a subgroup of \(P4m2\). Consequently, the non-magnetic orthorhombic distortion can survive in doped \(\text{LaFeAsO}\).

which, however, does not happen. Before reaching \(T_c\) the system becomes antiferromagnetic at 137 K, see Fig. 3.

The displacements of the Fe and O atoms in the non-magnetic system and in the antiferromagnetic state are depicted in Fig. 2 (b) of the present paper and Fig. 3 (c) of Ref. [7], respectively. They are almost identical, but there is a difference in \(z\) direction: In the non-magnetic system, the displacements realize the space group \(Pmm2\) and are periodic with \(T_3\) as given in Fig. 2 (b). In the antiferromagnetic system, on the other hand, they realize together with the magnetic moments the space group \(Pmn2\) and are no longer periodic with the lattice vector \(T_3\) in the non-magnetic system, but with the lattice vector \(T_3\) as given in Fig. 3 (c) of Ref. [7] which is twice as long as \(T_3\) in the non-magnetic system. Within the antiferromagnetic unit cell, however, a translation by \(T_3/2\) effects an inversion of the displacements.

The situation is changed in the doped system \(\text{LaFeAsO}_{1-x}\text{F}_x\) because the doping reduces the strong symmetry of the space group \(P4/nmm\). As substantiated in Sec. VI.1 the tetragonal group \(P4m2\) (115) is best adapted to the symmetry of the atomic-like electrons in weakly doped \(\text{LaFeAsO}\). Indeed, the degeneracies within the superconducting bands which suppress superconductivity in \(\text{LaFeAsO}\) are removed in \(P4m2\) and the active band of \(\text{LaFeAsO}\) (as denoted in Fig. 1 by the bold line) becomes a superconducting band. Thus, the electron system now is able to lower its correlation energy by producing the spin-boson interaction leading to superconductivity. This superconducting state is in fact experimentally established [9].

The antiferromagnetic state cannot survive in the doped system because the space group \(Pmn2\) of the antiferromagnetic state is not a subgroup of the space group \(P4m2\) of the atomic-like motion in the doped material, see the subgroup diagram in Table 2. As is experimentally observed, the antiferromagnetism actually disappears at relatively small doping levels between \(x = 0.03\) and 0.05 [5]. The non-magnetic orthorhombically distorted state, on the other hand, may readily survive in the doped system because the space group \(Pmm2\) of the non-magnetic distorted state is a subgroup of \(P4m2\). Also this phenomenon is experimentally established: the orthorhombic structural distortion extends beyond the antiferromagnetic phase and coexists with superconductivity [5], see Fig. 3.

Table 1 compiles all the space groups of \(\text{LaFeAsO}\) determined in the present paper and in Ref. [7] and Table 2 illustrates the subgroup relations of these space groups.

VII. CONCLUSIONS

In view of our present results on \(\text{LaFeAsO}\) and former results on the magnetic materials \(\text{Cr} [24]\), \(\text{Fe} [25]\), \(\text{La}_2\text{CuO}_4 [22]\), and \(\text{YBa}_2\text{Cu}_3\text{O}_6 [26]\), on the high-\(T_c\) superconductors \(\text{La}_2\text{CuO}_4 [22]\), \(\text{YBa}_2\text{Cu}_3\text{O}_7\), and \(\text{MgB}_2 [24]\), and on numerous elemental superconduc-
of LaFeAsO which is non-superconducting in the space straightforwardly corroborated by the physical properties of Cooper pairs, see Sec. II. This fundamental statement is system to possess eigenstates in which the electrons form state are determined by the “crystal-spin-1 bosons” me-

clusive. The special properties of the superconducting cause both, the superconducting and the antiferromag-

the antiferromagnetic state in the undoped material be-

LaFeAsO is not caused by the proximity of the system to conducting bands are straining forces operating in narrow, partly filled super-

tivity.

ACKNOWLEDGMENTS

We wish to thank Ernst Helmut Brandt for valuable discussion.

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Appendix A: Definition of superconducting bands

According to the definition in Ref. [14], an energy band of a given material is called “superconducting band” if the Bloch functions of this band

– can be unitarily transformed into \textit{spin-dependent} Wannier functions as defined by Eq. (A22) of Ref. [8] which are

– centered on one sort of the atoms of the material;
– symmetry-adapted to the (full) space group \(G\) of this material; and
– localized as well as possible [30];

– and cannot be unitarily transformed into usual, i.e., spin-independent Wannier functions with these properties.

Appendix B: Group-theoretical tables

| \(\Gamma\) | \(M\) | \(Z\) | \(A\) | \(R\) | \(X\) |
|-----------|------|------|------|------|------|
| Band 1    | \(\Gamma_1^+ + \Gamma_1^-\) | \(M_2\) | \(Z_3^+ + Z_2^-\) | \(A_4\) | \(R_1\) | \(X_1\) |
| Band 2    | \(\Gamma_2^+ + \Gamma_2^-\) | \(M_4\) | \(Z_3^+ + Z_2^-\) | \(A_2\) | \(R_2\) | \(X_2\) |
| Band 3    | \(\Gamma_3^+ + \Gamma_2^-\) | \(M_4\) | \(Z_3^+ + Z_4^-\) | \(A_2\) | \(R_1\) | \(X_1\) |
| Band 4    | \(\Gamma_4^+ + \Gamma_1^-\) | \(M_2\) | \(Z_3^+ + Z_3^-\) | \(A_4\) | \(R_2\) | \(X_2\) |

Notes to Table [B.1]

(i) Paramagnetic undoped LaFeAsO has the space group \(P4/nmm = \Gamma_4 D_{16}^4\) (129).
(ii) The energy bands belonging to the (spin-dependent) Wannier functions centered at the La or As atoms are not listed. The two branches of all these bands are degenerate at points \(M\) and \(A\), too.
(iii) The notations of the single-valued representations (a) are given in Table A.1 of Ref. [7].
(iv) The notations of the double-valued representations (b) may be identified from Table 6.13 in Ref. [21].
(v) Each row defines one band consisting of two branches, because there are two Fe atoms in the unit cell.
(vi) The bands are determined by Eq. (23) of Ref. [22].
(vii) Assume a band of the symmetry in any row of this table to exist in the band structure of LaFeAsO. Then the Bloch functions of this band can be unitarily transformed into Wannier functions that are

– localized as well as possible;
– centered at the Fe atoms; and
– symmetry-adapted to the space group \(P4/nmm\).

These Wannier function 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).
TABLE B.2. Character tables of the single-valued irreducible representations of the tetragonal space group \( P\bar{4}m2 = \Gamma_q D_{2d}^* (115) \).

| \( \Gamma(000), M(\frac{1}{2} \frac{1}{2} 0), \) | \( \sigma \) | \( S_{\sigma} \) | \( E \) | \( \{C_{2y}|0 \frac{1}{2} 0\} \) | \( \{C_{2x}|0 \frac{1}{2} 0\} \) | \( \{C_{4y}|0 \frac{1}{2} 0\} \) | \( \{\sigma_y|0 \frac{1}{2} 0\} \) |
| --- | --- | --- | --- | --- | --- | --- | --- |
| \( Z(00\frac{1}{4}) \), \( A(\frac{1}{4} \frac{1}{4} \frac{1}{4}) \) | \( \{E|000\} \) | \( \{C_{2y}|\frac{1}{2} \frac{1}{2} 0\} \) | \( \{\sigma_y|\frac{1}{2} \frac{1}{2} 0\} \) |
| \( \Gamma_1, M_1, Z_1, A_1 \) | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| \( \Gamma_2, M_2, Z_2, A_2 \) | 1 | 1 | 1 | -1 | -1 | 1 | 1 |
| \( \Gamma_3, M_3, Z_3, A_3 \) | 1 | 1 | -1 | 1 | -1 | 1 | 1 |
| \( \Gamma_4, M_4, Z_4, A_4 \) | 1 | 1 | -1 | -1 | 1 | 1 | 1 |
| \( \Gamma_5, M_5, Z_5, A_5 \) | 2 | -2 | 0 | 0 | 0 | 0 | 0 |

Notes to Table B.2

(i) The group \( P\bar{4}m2 \) is optimally adapted to the symmetry of atomic-like electrons at the Fe sites in weakly doped LaFeAsO. (ii) The character tables are determined from Table 5.7 in Ref. [21], where the symmetry operations given in Table 5.7 of Ref. [21] are changed into the operations used in this paper as described in the notes to Table B.2. (iii) The group \( P\bar{4}m2 \) is symmorphic. Hence, the point group operations are, on their own, symmetry operations of the crystal. Nevertheless, in this paper, the point group operations are associated with translations in consequence of the unusual position of our coordinate system given in Fig. 2 (a).

TABLE B.3. Character tables of the double-valued irreducible representations of the space group \( P\bar{4}m2 \).

| \( \Gamma(000), \) | \( M(\frac{1}{2} \frac{1}{2} 0), \) | \( \{C_{2y}|\frac{1}{2} \frac{1}{2} 0\} \) | \( \{\sigma_y|0 \frac{1}{2} 0\} \) |
| --- | --- | --- | --- |
| \( Z(00\frac{1}{4}), A(\frac{1}{4} \frac{1}{4} \frac{1}{4}) \) | \( \{E|000\} \) | \( \{S_{\sigma}|\frac{1}{2} \frac{1}{2} 0\} \) | \( \{\sigma_y|\frac{1}{2} \frac{1}{2} 0\} \) |
| \( \{C_{2y}|\frac{1}{2} \frac{1}{2} 0\} \) | \( \{C_{2x}|0 \frac{1}{2} 0\} \) | \( \{\sigma_y|0 \frac{1}{2} 0\} \) |
| \( \Gamma_6, M_6, Z_6, A_6 \) | 2 | -2 | 0 | \( -\sqrt{2} \) | \( -\sqrt{2} \) | 0 | 0 |
| \( \Gamma_7, M_7, Z_7, A_7 \) | 2 | -2 | 0 | \( \sqrt{2} \) | \( \sqrt{2} \) | 0 | 0 |

Note to Table B.3

(i) The character tables are determined from Table 6.13 in Ref. [21], cf. the notes to Table B.2.
TABLE B.4. Compatibility relations between the space groups \( P4/nmm \) and \( P\overline{4}m2 \).

| \( \Gamma \), \( Z \) | \( M \), \( A \) | \( R \), \( X \) |
|---------------------|-----------------|-----------------|
| \( R_1^+ \) \( R_2^+ \) \( R_3^+ \) \( R_4^+ \) \( R_5^+ \) | \( R_1 \) \( R_2 \) \( R_3 \) \( R_4 \) | \( R_1 \) \( R_2 \) |
| \( R_1 \) \( R_2 \) \( R_3 \) \( R_4 \) \( R_5 \) | \( R_5 \) \( R_1 + R_3 \) \( R_2 + R_4 \) | \( R_1 + R_4 \) \( R_3 + R_2 \) |

Notes to Table B.4

(i) The Brillouin zones for \( P4/nmm \) and \( P\overline{4}m2 \) are identical.

(ii) The letter \( R \) stands for the letter denoting the relevant point of symmetry. For example, at point \( M \) the representations \( R_1, R_2, \ldots \) stand for \( M_1, M_2, \ldots \).

(iii) The upper and lower rows list the representations of \( P4/nmm \) and \( P\overline{4}m2 \), respectively. The representations in the same column are compatible in the following sense: Bloch functions that are basis functions of a representation \( D_i \) in the upper row can be unitarily transformed into the basis functions of the representation given below \( D_i \).

(iv) The compatibility relations are determined in the way described in Ref. [31].

(v) The representations are labeled as given in Table A.1 of Ref. [7] and Table B.2 respectively.

TABLE B.5. Compatibility relations between the single-valued (upper row) and double-valued (lower row) representations of the space group \( P\overline{4}m2 \).

| \( \Gamma \), \( Z \), \( M \), \( A \) | \( R \), \( X \) |
|---------------------|-----------------|
| \( R_1 \) \( R_2 \) \( R_3 \) \( R_4 \) \( R_5 \) | \( R_1 \) \( R_3 \) \( R_2 \) \( R_4 \) |
| \( R_5 \) \( R_6 \) \( R_7 \) \( R_7 + R_7 \) | \( R_5 \) \( R_5 \) \( R_3 \) \( R_5 \) |

Notes to Table B.5

(i) The letter \( R \) stands for the letter denoting the relevant point of symmetry. For example, at point \( M \) the representations \( R_1, R_2, \ldots \) stand for \( M_1, M_2, \ldots \).

(ii) The single-valued and double-valued representations are listed in Tables B.2 and B.3 respectively.

(iii) Each column lists the double-valued representation \( R_1 \times D_{1/2} \) below the single-valued representation \( R_i \), where \( D_{1/2} \) denotes the two-dimensional double-valued representation of the three-dimensional rotation group \( O(3) \) given, e.g., in Table 6.1 of Ref. [21].
TABLE B.6. Single- and double-valued representations of all the energy bands in the tetragonal space group \( P\overline{4}m2 = \Gamma_4 D_{2d}^2 \) (115) with symmetry-adapted and optimally localized (spin-dependent) Wannier functions centered at the Fe atoms.

(a) Single-valued representations

| \( \Gamma \) | \( \mathcal{M} \) | \( Z \) | \( \mathcal{A} \) | \( R \) | \( X \) |
|---|---|---|---|---|---|
| Band 1 | \( \Gamma_1 \) | \( M_1 + M_3 \) | \( 2Z_4 \) | \( A_2 + A_4 \) | \( R_1 + R_4 \) | \( X_1 + X_4 \) |
| Band 2 | \( \Gamma_2 \) | \( M_2 + M_4 \) | \( 2Z_3 \) | \( A_1 + A_3 \) | \( R_3 + R_2 \) | \( X_3 + X_2 \) |
| Band 3 | \( \Gamma_3 \) | \( M_1 + M_3 \) | \( 2Z_2 \) | \( A_2 + A_4 \) | \( R_3 + R_2 \) | \( X_3 + X_2 \) |
| Band 4 | \( \Gamma_4 \) | \( M_2 + M_4 \) | \( 2Z_1 \) | \( A_1 + A_3 \) | \( R_1 + R_4 \) | \( X_1 + X_4 \) |

(b) Double-valued representations

| \( \Gamma \) | \( \mathcal{M} \) | \( Z \) | \( \mathcal{A} \) | \( R \) | \( X \) |
|---|---|---|---|---|---|
| Band 1 | \( \Gamma_6 \) | \( M_6 + M_7 \) | \( 2Z_7 \) | \( A_6 + A_7 \) | \( 2R_5 \) | \( 2X_5 \) |
| Band 2 | \( \Gamma_7 \) | \( M_6 + M_7 \) | \( 2Z_6 \) | \( A_6 + A_7 \) | \( 2R_5 \) | \( 2X_5 \) |

Notes to Table B.6

(i) The notations of the single-valued and double-valued representations are given in Tables B.2 and B.3, respectively.
(ii) Each row defines one band consisting of two branches, because there are two Fe atoms in the unit cell.
(iii) The bands are determined by Eq. (23) of Ref. [22].
(iv) Assume a band of the symmetry in any row of this table to exist in the band structure of LaFeAsO. Then the Bloch functions of this band can be unitarily transformed into Wannier functions that are

- localized as well as possible;
- centered at the Fe atoms; and
- symmetry-adapted to the space group \( P\overline{4}m2 \).

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).