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The origin of a flat band

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Abstract

The origin of a "flat band" as defined in the "flat band–steep band" model for superconductivity has been studied. A "local inversion center" is derived mathematically as the necessary and sufficient condition for an occurrence of a "flat band" at an arbitrary $\vec{k}$ point. From the $\vec{k}$-dependent part of $E(\vec{k}j)$, a "pseudo-inversion center" is demonstrated to be a sufficient condition based on the Patterson symmetry. The chemical bonding origin of a "flat band" is also studied analytically with a tight-binding approach.

Keywords: Flat band; Van Hove singularity; Chemical bonding; Tight binding; Super-conductivity

1. Introduction

Superconductivity represents a coherent state of pairwise correlated conduction electrons. In a metal the tendency for pairwise localization of electrons is counteracted by the itinerant character of the majority of the conduction electrons as otherwise a non-conducting state would result. In a series of papers we have pointed out that this pairwise localization vs. mobility picture of electrons reflects itself in the band structure as a "flat band–steep band" scenario [1–4] which is a necessary though not a sufficient condition for a metal to become a superconductor [5,6]. A "flat band" as defined on the basis of band theory in Ref. [2] refers to close to zero-velocity points (or extended regions) in momentum space of electrons near the Fermi level. As the "flat band" plays a crucial role in our model and has not yet been studied in our previous work, we investigate here the general conditions for the occurrence of a "flat band" in a band structure. Some earlier attempts have been made to find such conditions in terms of the occurrence of van Hove singularities and zero-slope points by Kudryavtseva [7] and Cracknell [8]. However, such efforts have only given some sufficient conditions related with point group symmetries. In this work, we start with a general expression of an electronic energy spectrum in a solid and then study its local symmetry in momentum space and its relation to the chemical bonding in a solid.

2. Description of the method

The energy of an electron in a crystalline solid can be expressed as an eigenvalue of the Hamiltonian of the system

$$E(\vec{k}j) = \langle \vec{k}j|\hat{H}|\vec{k}j\rangle, \tag{1}$$

where $|\vec{k}j\rangle$ is the eigenstate of operator $\hat{H}$ in Bloch representation with $\vec{k}$ being the wave vector of an electron and j the band index. Now we use the Wannier representation [9] of the eigenstate, namely

$$|\vec{k}j\rangle = \frac{1}{\sqrt{N}}\sum_{\vec{l}} e^{i\vec{k}\vec{l}}|\vec{l}j\rangle, \tag{2}$$

where N is the total number of primitive unit cells in the crystal, and $\vec{l}$ is the lattice vector in real space. By using Eq. (2) and the translational symmetry of the direct lattice, Eq. (1) can be written as

$$E(\vec{k}j) = \frac{1}{N}\sum_{\vec{l}} e^{i\vec{k}\vec{l}} H_j(\vec{l}), \tag{3}$$

where $H_j(\vec{l}) = \langle \vec{l}_1 j|\hat{H}|\vec{l}_2 j\rangle$ with $\vec{l} = \vec{l}_1 - \vec{l}_2$ is the hopping integral between lattice point $\vec{l}_1$ and $\vec{l}_2$, which

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generally represents the inter-cell interactions ($\vec{l}_1 \neq \vec{l}_1$) or the on-site interactions ($\vec{l}_1 = \vec{l}_1$). With formula (3), it is convenient to calculate the group velocity of an electron in the first Brillouin zone (BZ) and thus determine the positions of "flat bands" and "steep bands" in the BZ.

The concept "flat/steep band" as defined in our earlier work [2], relies on the group velocity which assumes a fixed band indexing scheme. Any changes such as choosing a supercell or lowering the symmetry etc. which result in a new indexing of bands and thus change the "flatness" of a band should be avoided in one analysis, because such changes do not change the physics of the system.

The group velocity $\vec{v}$ of an electron is defined as [10]

$$\vec{v} = \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\vec{k}j). \tag{4}$$

By substituting Eq. (3) in Eq. (4) we obtain for $\vec{v}$

$$\vec{v} = \frac{1}{N\hbar}\sum_{\vec{l}} \mathrm{i}\,\vec{l}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{l}} H_j(\vec{l}). \tag{5}$$

The summation term in Eq. (5) contains two factors. The first one is $\mathrm{i}\,\vec{l}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{l}}$ which is $\vec{k}$ and $\vec{l}$ dependent, while the second one, $H_j(\vec{l})$, has no $\vec{k}$ dependence. It is obvious that both these two factors can independently or cooperatively produce a "flat band" ($\vec{v}(\vec{k}j) \approx 0$). In order to see the influence of the first factor clearly, we take the tight-binding approximation of Eq. (3), namely include only the zero and first-order terms in the right hand of Eq. (3), which under the isotropic approximation leads to

$$E(\vec{k}j) = H_j(0) + H_j(1)\sum_{\vec{\rho}} \mathrm{e}^{\mathrm{i}\vec{k}\vec{\rho}}. \tag{6}$$

The summation index $\vec{\rho}$ runs over all of the nearest-neighbor lattice vectors of one lattice point, and $H_j(1)$ is the isotropic nearest-neighbor interaction. From Eq. (6) the velocity $\vec{v}(\vec{k}j)$ can be calculated as

$$\vec{v} = \frac{1}{\hbar}H(1)\sum_{\vec{\rho}} \mathrm{i}\,\vec{\rho}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{\rho}}. \tag{7}$$

Formula (7) can be directly used to determine the position of a "flat band". For example, if a lattice has a center of symmetry then (7) can be simplified as

$$\vec{v} = -\frac{1}{\hbar}H(1)\sum_{\vec{\rho}} \vec{\rho}\,\sin(\vec{k}\vec{\rho}). \tag{8}$$

As $\vec{\rho}$ runs only over the nearest neighboring lattice points, it can only be one of the primitive unit vectors ($\vec{t}_i$, $i = 1, 2, 3$). Considering the definition of the BZ and the fact that $E(\vec{k} + \vec{K}) = E(\vec{k})$, we know that $\vec{k}\vec{\rho}$ must be $n\pi$ ($n = 0, \pm 1 \ldots$) to make $\vec{v} = 0$, which requires that $\vec{k}$ lies at the BZ center or boundary. For more general cases, it is difficult to directly use the explicit formula (5) to determine the position of "flat bands" in the whole BZ.

Cracknell's "zero-slope" conditions only reflect the contribution of the first factor ($\mathrm{i}\,\vec{l}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{l}}$) in formula (5), which are just some sufficient conditions for the occurrence of "flat bands". To find the necessary and sufficient conditions for a "flat band" to occur in the BZ, we analyze the structure of $E(\vec{k}j)$ in the neighborhood of $\vec{k}$. For simplicity, we omit the band index j in the following derivation. By using a Taylor expansion, we have

$$E(\vec{k} + \delta\vec{k}) = E(\vec{k}) + \delta\vec{k}\nabla E(\vec{k}) + \mathrm{O}^2(\delta\vec{k}), \tag{9a}$$

$$E(\vec{k} - \delta\vec{k}) = E(\vec{k}) - \delta\vec{k}\nabla E(\vec{k}) + \mathrm{O}^2(\delta\vec{k}) \tag{9b}$$

($\mathrm{O}^2(\delta\vec{k})$, higher order terms). From (9) a directional derivative along an arbitrary direction $\vec{u} = \delta\vec{k}/|\delta\vec{k}|$ can be calculated as

$$\vec{u}\nabla E(\vec{k}) = \lim_{|\delta k|\to 0} \frac{E(k + \delta k) - E(k - \delta k)}{2|\delta k|}. \tag{10}$$

The gradient of $E(\vec{k})$ in Eqs. (9) and (10) can be written in its component form in the Cartesian coordinate system with $\vec{e}_i$ ($i = 1, 2, 3$) being the basis vectors:

$$\begin{aligned}\nabla E(\vec{k}) &= \frac{\partial E(\vec{k})}{\partial k_x}\vec{e}_1 + \frac{\partial E(\vec{k})}{\partial k_y}\vec{e}_2 + \frac{\partial E(\vec{k})}{\partial k_z}\vec{e}_3 \\ &= \xi_1\vec{e}_1 + \xi_2\vec{e}_2 + \xi_3\vec{e}_3.\end{aligned} \tag{11}$$

To find ξ_1, ξ_2 and ξ_3 we use Eq. (10) and multiply Eq. (11) with three arbitrarily chosen independent unit vectors $\vec{u}_i$ (here $i = 1, 2, 3$, does not represent a Cartesian component) and obtain

$$\begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{pmatrix}\begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \begin{pmatrix} d_1 \\ d_2 \\ d_3 \end{pmatrix}, \tag{12}$$

where the derivative d_i in $\vec{u}_i$ ($i = 1, 2, 3$) direction is defined as

$$d_i = \lim_{|\delta\vec{k}_i|\to 0} \frac{E(\vec{k} + \vec{u}_i|\delta\vec{k}_i|) - E(\vec{k} - \vec{u}_i|\delta\vec{k}_i|)}{2|\delta\vec{k}_i|}. \tag{13}$$

According to Gramers rule the coefficients are: $\xi_1 = \Delta_1/\Delta$, $\xi_2 = \Delta_2/\Delta$, $\xi_3 = \Delta_3/\Delta$ with

$$\begin{aligned}\Delta &= u_1 \cdot (\vec{u}_2 \times \vec{u}_3), \\ \Delta_1 &= [d_1(\vec{u}_2 \times \vec{u}_3) + d_2(\vec{u}_1 \times \vec{u}_3) + d_3(\vec{u}_1 \times \vec{u}_2)]\vec{e}_1, \\ \Delta_2 &= [d_1(\vec{u}_2 \times \vec{u}_3) + d_2(\vec{u}_1 \times \vec{u}_3) + d_3(\vec{u}_1 \times \vec{u}_2)]\vec{e}_2, \\ \Delta_3 &= [d_1(\vec{u}_2 \times \vec{u}_3) + d_2(\vec{u}_1 \times \vec{u}_3) + d_3(\vec{u}_1 \times \vec{u}_2)]\vec{e}_3.\end{aligned}$$

For clarity we introduce $\vec{g}_i = \vec{u}_j \times \vec{u}_k / \vec{u}_1(\vec{u}_2 \times \vec{u}_3)$ $(i,j,k = 1,2,3)$.

Then we obtain

$$\xi_1 = \frac{\Delta_1}{\Delta} = (d_1\vec{g}_1 + d_2\vec{g}_2 + d_3\vec{g}_3)\vec{e}_1,$$
$$\xi_2 = \frac{\Delta_1}{\Delta} = (d_1\vec{g}_1 + d_2\vec{g}_2 + d_3\vec{g}_3)\vec{e}_2, \quad (14)$$
$$\xi_3 = \frac{\Delta_3}{\Delta} = (d_1\vec{g}_1 + d_2\vec{g}_2 + d_3\vec{g}_3)\vec{e}_3.$$

As $\vec{e}_i \cdot \vec{e}_j = \delta_{ij}$, it follows from these three equations that if and only if d_1, d_2 and d_3 are all zero, ξ_1, ξ_2 and ξ_3 can all be zero which is the condition for the presence of a flat band. Considering Eq. (13) and the fact that $\vec{u}_i$ $(i = 1,2,3)$ is chosen arbitrarily and independent of each other, $d_i = 0$ thus implies that *there exists an local inversion center for $E(\vec{k})$ at $\vec{k}$ with respect to its neighborhood*. This is the necessary and sufficient condition for the existence of a "flat band" at an arbitrary $\vec{k}$ point. It should be stressed that this is a general conclusion, because in our derivation we do not assume any conditions for $E(\vec{k})$ except that it is differentiable with respect to $\vec{k}$. This "inversion center" at $\vec{k}$ is local with respect to $E(\vec{k})$, which has nothing to do with the intrinsic center of symmetry of the reciprocal space.

It is obvious from formula (13), that the necessary and sufficient condition will easily be satisfied, if there exists some symmetry elements at $\vec{k}$. The symmetry properties of $E(\vec{k})$ have already been studied before [11–13], but for a better understanding and explanation, a simple demonstration is given here. Suppose that $\{\alpha|\upsilon\}$ is a space group operation, then its inverse operation is $\{\alpha|\upsilon\}^{-1} = \{\alpha^{-1}|-\alpha^{-1}\upsilon\}$, and $\hat{O}(\{\alpha|\upsilon\})$ is the corresponding symmetry operator. Hamiltonian $\hat{H}$ is invariant under the symmetry operation, so is its eigenvalue $E(\vec{kj})$, namely $\hat{O}E(\vec{kj}) = E(\vec{kj})$. Now we apply $\hat{O}$ to Eq. (1) and use the coordinate representation of the state vector. Then we obtain

$$\hat{O}E(\vec{kj}) = \int \langle \vec{kj}|\vec{r}'\rangle \hat{H} \langle \vec{r}'|\vec{kj}\rangle \, \mathrm{d}\vec{r}',$$

with $\vec{r}' = \alpha^{-1}\vec{r} - \alpha^{-1}\upsilon$

$$= \int \langle \alpha\vec{kj}|\vec{r}\rangle \hat{H} \langle \vec{r}|\alpha\vec{kj}\rangle \, \mathrm{d}\vec{r}$$
$$= E(\alpha\vec{kj}) = E(\vec{kj}). \quad (15)$$

Formula (15) tells us, that the non-symmorphic operations υ in $\{\alpha|\upsilon\}$ do not exist. As $E(\vec{kj}) = E(\vec{k} + \vec{kj})$ because of the translational symmetry and $E(\vec{kj}) = E(-\vec{kj})$, which is due to the time reversal symmetry, $E(\vec{kj})$ *has the symmetry of the Patterson group*. As a consequence we can consider the site symmetry in reciprocal space as in real space. From Eqs. (13) and (14), it is evident that if $\vec{k}$ lies at a *Wyckoff* position of the corresponding Patterson group, where there exists a third order *pseudo-inversion center then the flat band condition is fulfilled*. Here an *n*th order *pseudo-inversion* center means that the inversion symmetry holds only for *n* directions defined by linearly independent vectors, not necessarily for all possible directions as for a real inversion center. The pseudo-inversion center also refers to the actual situation where only approximate symmetry exists due to structure modulation or distortion. This condition will guarantee the existence of a local "inversion center" as discussed above. The pseudo-inversion symmetry self-evidently includes all of the special cases $P'(\vec{k}_0)$ listed by Cracknell on the basis of point group symmetries [8]. We thus establish a simple procedure to determine a possible "flat band" at any $\vec{k}$ point by using just the International Tables of Crystallography. This "pseudo-inversion" symmetry results from the Patterson group, and therefore represents a global symmetry of the isoenergy surface. It must be pointed out that this global pseudo-inversion center symmetry differs substantially from the "local inversion center" discussed before. It implicitly excludes the case where Cracknell's symmetry condition is satisfied but $E(\mathbf{k}j)$ is non-differentiable.

In the last part, we mainly have analyzed the symmetry conditions resulting in "flat bands" as reflected by the contribution of the factor $\mathrm{i}\vec{l}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{l}}$ in Eq. (5), which does not involve any chemical constituents of the structure. The latter, however, is even more important in deciding the physical and chemical properties. Now, we study the role of $H_j(\vec{l})$ in Eq. (5) which provides some other conditions for flattening a band. As already mentioned above, $H_j(\vec{l})$ represents the inter-cell interactions, which are difficult to deal with when there is more than one atom in the primitive unit cell. To see how chemical bonding influences the flatness of a band, we expand the state vector $|\vec{k}j\rangle$ explicitly on the basis atoms as

$$\left|\vec{k}j\right\rangle = \sum_{\tau L} \left|\chi_{\tau L}^{\vec{k}}\right\rangle A_{\tau L}^{\vec{k}j}, \quad (16)$$

where τ is the atomic position vector, L is a shorthand symbol of quantum number l and m, χ represents the basis function and $A_{\tau L}^{kj}$ is the eigenvector. With (16) $E(\vec{kj})$ can be expressed as

$$E(\vec{k}j) = \sum_{\tau L, \tau'+\vec{T}L'} H_{\tau L, \tau'+\vec{T}L'} A_{\tau L}^{\vec{k}j*} A_{\tau'+\vec{T}L'}^{\vec{k}j}, \quad (17)$$

where $H_{\tau L, \tau'+\vec{T}L'}$ is a Hamiltonian matrix element between the orbital L of atom τ and L' of atom $\tau' + \vec{T}$ with $\vec{T}$ being the lattice vector. In fact the summation term in Eq. (17) is nothing else but the $\vec{k}, j$ dependent COHP matrix elements proposed by Dronskowski and Blöchl who have used a real space representation [14].

From (17) we calculate the velocity as

$$\vec{v} = \frac{1}{\hbar} \sum_{\tau L, \tau' + \vec{T} L'} H_{\tau L, \tau' + \vec{T} L'} \nabla_k \left(A^{\vec{k}j^*}_{\tau L} A^{\vec{k}j}_{\tau' + \vec{T} L'} \right). \quad (18)$$

Since COHP measures the covalent bonding strength, generally speaking a weak covalent bonding (small $H_{\tau L, \tau' + \vec{T} L'}$) *between the atoms in different unit cells will lead to a small* $\vec{v}$ *and thus produces a flat band*. A typical example of this rule is the case of molecular crystals or ionic crystals where there is nearly no covalence between the molecules or ions, and the bands are indeed rather flat. Such a correlation was also mentioned by Hoffmann based on the orbital overlap argument [15]. A rather extended "flat band" derived from the non-bonding orbital can be found in Wheeler et al.'s work [16].

3. Discussion and conclusion

From the definition of a "flat band" and the general expression for $E(\vec{k}j)$, we have found two sources that result in a "flat band", one of which is $\vec{k}$-dependent, the other $\vec{k}$-independent. Some sufficient conditions are derived from the $\vec{k}$-dependent part by means of the tight-binding model and the site-symmetry of the Patterson group of $E(\vec{k})$, that can be generalized as a *third order pseudo-inversion center* at $\vec{k}$. The analysis based on the $\vec{k}$-independent part connects *weak covalent bonding and the flat band*. The analytical studies of $E(\vec{k}j)$ result in the necessary and sufficient condition for the occurrence of a "flat band", that is the *local inversion center* at $\vec{k}$.

It should be pointed out that the sufficient conditions given above are for the ideal situation with respect to symmetry. In practice one may meet a $<$third order pseudo-inversion center or a strongly anisotropic structure with respect to covalent bonding. In these cases the "flat bands" exist only along some specific directions. Besides, because of the pseudo-symmetry, caused by structural modulation or distortion or any other reasons, the extended Brillouin zone corresponding to the pseudo-symmetry may be used to represent the bands. In these cases, "flat bands" originated from the above two reasons may occur inside the zone. An interesting example can be found in a "helical face-sharing tetrahedron chain" model [17]. From the above discussion , it is also clear that the "flat band" resulted from the "weak covalent bonding" condition should have a larger extension than that from the "pseudo-inversion center", because the former condition is $\vec{k}$-independent.

As an illustration of these principles, we take α-Hg as an example. It has space group $R\bar{3}m$, and the Patterson group is also $R\bar{3}m$. From the listed Wyckoff positions we know that inversion centers exist at $a(\Gamma)$, $b(Z), d(L), e(F)$, respectively, so "flat bands" should exist at these $\vec{k}$ points, which is consistent with our numerical calculations [2]. Another interesting example is MgB_2 [18]. Fig. 1 shows the band structure calculated with the TB-LMTO method. As MgB_2 has a Patterson symmetry of $P6/mmm$, the condition of "third order pseudo-inversion center" is automatically satisfied at a $(\Gamma), b(A)$ and $f(M)$, respectively.

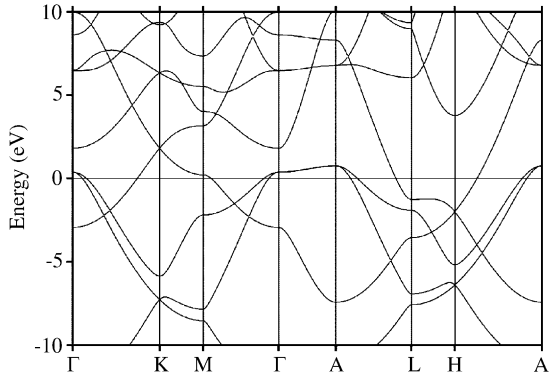

Fig. 1. Band structure of MgB_2 calculated with the TB-LMTO method shows the "flat band–steep band" character around the Fermi level.

As the $\Gamma - A$ line has C_{6v} symmetry, only a second order pseudo-inversion center exists on it. The **k** points on this line are all extremal points with respect to lines in [001] plane, while for $\mathbf{k}_z$ direction there is no "pseudo-inversion center", so $\partial E_{\mathbf{k}j}/\partial k_z \neq 0$. Nevertheless, as the $B\cdots B$ interlayer covalent bonding is rather weak the z-component of the group velocity, $\partial E_{kj}/\partial k_z$, is very small. Therefore it is the symmetry and the 2D character of the structure that produce the "flat band" from Γ to A. It should be noted that what we can see from Fig. 1 is just the effect of small $\partial E_{kj}/\partial k_z$. To really understand the flatness of band 3, 4 from Γ to A, one needs to inspect the electronic velocities for these states. Other "flat bands" exist in Fig. 1, however since they are far away from the Fermi level they are not included in our study. In a word, "flat bands" produced by symmetry and "weak covalent" bonding simultaneously occur in MgB_2 and lie close to the Fermi level. This character together with the "steep band" crossing the Fermi level make MgB_2 a model compound of our "flat band/ steep band" scenario for superconductivity.

As a final remark we draw attention to the fact that we treat the "flat band" independently with respect to the position of the Fermi level. Of course, for a "flat band" to play a role in the "flat band–steep band" scenario of superconductivity, it has to be close to the Fermi level. In that sense the scenario provides a tool in the search for new superconductors.

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References

[1] A. Simon, Angew. Chem. 109 (1997) 1873;
A. Simon, Angew. Chem. Int. Ed. Engl. 36 (1997) 1788.
[2] S. Deng, A. Simon, J. Köhler, Angew. Chem. 110 (1998) 664;
S. Deng, A. Simon, J. Köhler, Angew. Chem. Int. Ed. Engl. 37 (1998) 640.
[3] S. Deng, A. Simon, J. Köhler, Solid State Sciences 2 (2000) 31.
[4] S. Deng, A. Simon, J. Köhler, J. Phys. Chem. Solids 62 (2001) 1441.
[5] S. Deng, A. Simon, J. Köhler, J. Amer. Chem. Soc. 124 (2002) 10712.
[6] S. Deng, J. Köhler, A. Simon, J. Supercond. 15 (2002) 635.
[7] N.V. Kudryavtseva, Sov. Phys. Solid State 9 (1967) 1850;
N.V. Kudryavtseva, Sov. Phys. Solid State 10 (1968) 1280;
N.V. Kudryavtseva, Sov. Phys. Solid State 11 (1969) 840.
[8] A.P. Cracknell, J. Phys. C: Solid State Phys. 6 (1973) 826;
A.P. Cracknell, J. Phys. C: Solid State Phys. 6 (1973) 841.
[9] G.H. Wannier, Phys. Rev. 32 (1937) 191.
[10] M. Lax, Symmetry Principles in Solid State and Molecular Physics, Wiley, New York, 1974.
[11] E.P. Wigner, Group Theory and its Application to the Quantum Mechanics of Atomic spectra, Academic Press, New York, 1959.
[12] C.J. Bradely, A.P. Cracknell, The Mathematical Theory of Symmetry in Solids, Clarendon, Oxford, 1972.
[13] J.P. Jan, Can. J. Phys. 50 (1972) 925.
[14] R. Dronskowski, P.E. Blöchl, J. Phys. Chem. 97 (1993) 8617.
[15] R. Hoffmann, Rev. Mod. Phys. 60 (1988) 601.
[16] R.A. Wheeler, M.-H. Whangbo, T. Hughbanks, R. Hoffmann, J.K. Burdett, T.A. Albright, J. Am. Chem. Soc. 112 (1990) 3784.
[17] C. Zheng, R. Hoffmann, D.R. Nelson, J. Am. Chem. Soc. 112 (1990) 3784.
[18] S. Deng, A. Simon, J. Köhler, J. Supercond. 16 (2003) 477.