固体中的电子共振价键态和高温超导

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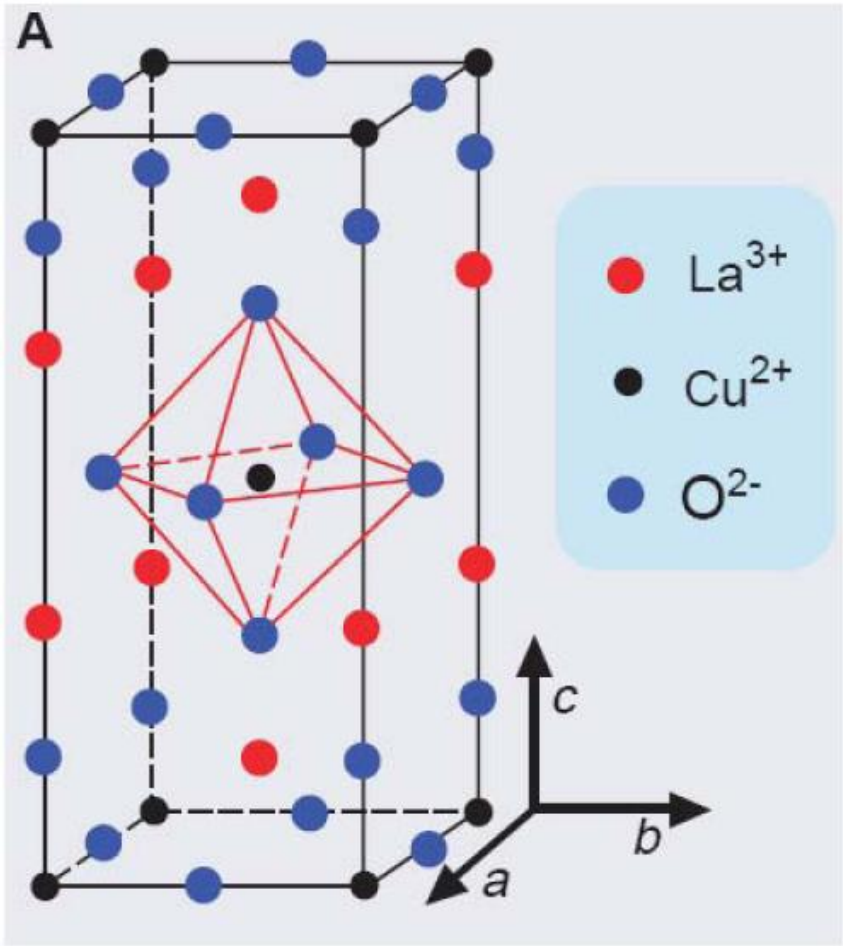
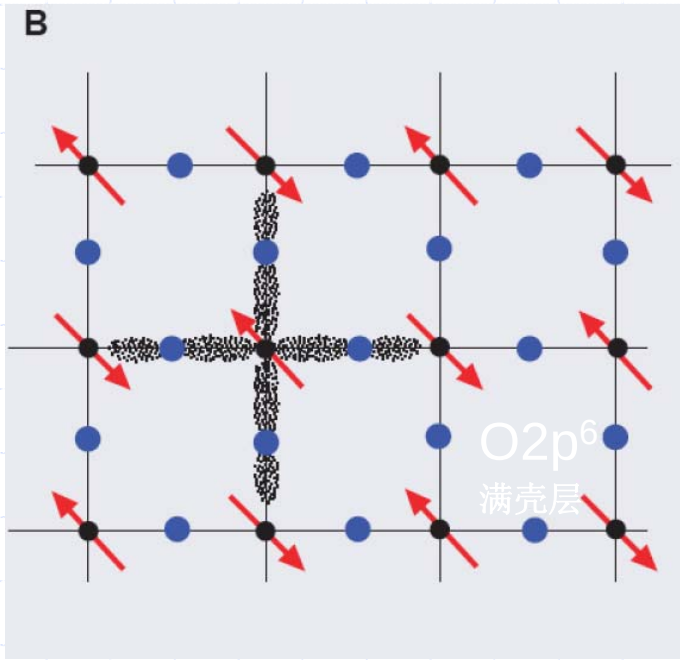
La_2CuO_4 的晶体结构和磁结构



晶体结构

Cu^{2+} 离子的电子组态： $3d^9$

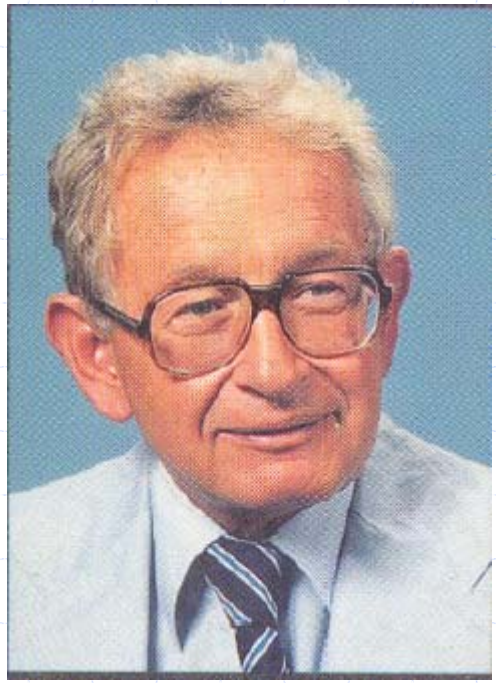


每个铜格位上有自旋 $S = 1/2$

The Resonating Valence Bond State in La_2CuO_4 and Superconductivity

P. W. ANDERSON

The oxide superconductors, particularly those recently discovered that are based on La_2CuO_4, have a set of peculiarities that suggest a common, unique mechanism: they tend in every case to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. This insulating phase is proposed to be the long-sought "resonating-valence-bond" state or "quantum spin liquid" hypothesized in 1973. This insulating magnetic phase is favored by low spin, low dimensionality, and magnetic frustration. The preexisting magnetic singlet pairs of the insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly. The mechanism for superconductivity is hence predominantly electronic and magnetic, although weak phonon interactions may favor the state. Many unusual properties are predicted, especially of the insulating state.



RECENTLY HIGH-TEMPERATURE SUperconductivity has been observed in a number of doped lanthanum copper oxides near a metal-insulator transition (*1*), a pattern exhibited previously by $(Ba,Pb)BiO_3$ (*2*). The crystal structure suggests that the Cu^{2+} is in an $S = 1/2$, orbitally nondegenerate state, strongly hybridized with the surrounding oxygen *p*-levels, and this is in agreement with high-temperature

to reexamine the idea of the "resonating valence-bond" (RVB) state (*5*).

Early doubts about the nature of the ground state of the antiferromagnetic Heisenberg Hamiltonian

$$H = J\sum_{i\neq j} \vec{S}_i \cdot \vec{S}_j \qquad (1)$$

of Hulthén (*6*) and Marshall (*7*) (where $\vec{S}_i$ is the spin at site i and $i\neq j$ indicates summa-

Anderson P W, Science **235** , 1196

The Nature of the Interatomic Forces in Metals

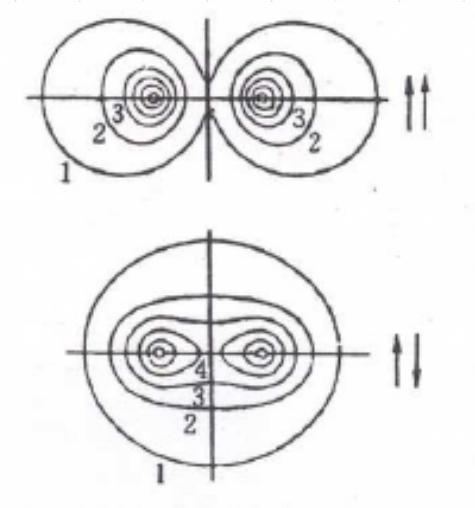
LINUS PAULING
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California
(Received October 10, 1938)

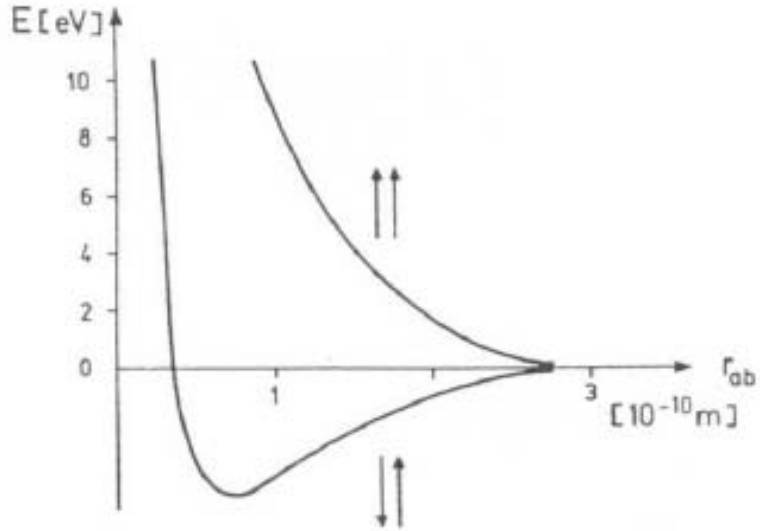
It has been generally assumed that in the transition elements (Fe, Co, Ni, Cu, etc.) the 3*d* shell is filled with ten electrons or is nearly filled, and that the *d* electrons make no significant contribution to the cohesive forces in metals. Evidence is presented here to show that about half of the *d* orbitals (2.56 of the total of 5) are involved in bond formation, through hybridization with the 4*s* and 4*p* orbitals, and that the number of covalent bonds resonating among the available interatomic positions increases from one to nearly six in the sequence K, Ca, Sc, Ti, V, Cr, remains nearly constant from Cr to Ni, and begins to decrease with Cu. The remaining 2.44 *d* orbitals, with very small interatomic overlapping, are occupied by nonbonding electrons which are mainly responsible for the ferromagnetic and paramagnetic properties of the metals. This point of view provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as interatomic distance, characteristic temperature, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements iron, cobalt, and nickel and their alloys. It is also shown to provide a reason for the occurrence of the positive exchange integrals which give rise to ferromagnetism.

DURING the year 1926–1927 I had the great privilege of working as a Guggenheim Fellow in Munich under the direction of Professor Arnold Sommerfeld. At that time he was interested in the systematization of the new quantum mechanics and its application to problems of spectroscopy and atomic structure. It was not until the following year, after the pioneer work of Pauli[1] on the small temperature-independent paramagnetism of the alkali metals, that Professor Sommerfeld and his students began their development of the quantum-mechanical theory of the metallic state.[2] The extension of the theory to other elements has also been attempted.

In recent years I have formed, on the basis mainly of empirical arguments, a conception of the nature of the interatomic forces in metals which has some novel features. According to this view, the metallic bond is very closely related to the ordinary covalent or electron-pair bond; some of the electrons of an atom in a metal are involved with those of neighboring atoms in the interaction described as covalent-bond formation, with the bonds resonating among the

共价键系统－氢分子



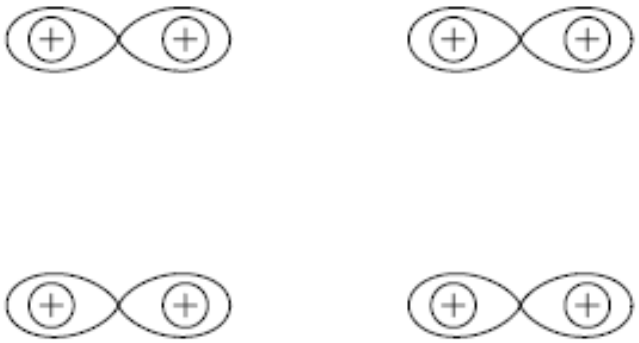


氢分子中反键的电子轨道（上图）和成键的电子轨道（下图）

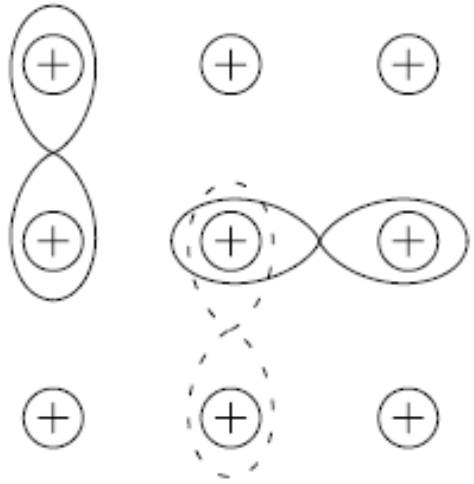
：氢分子中两电子自旋相反形成成键，自旋平行形成反键.

泡令建议的共振价键态

共价键晶体 – 氟



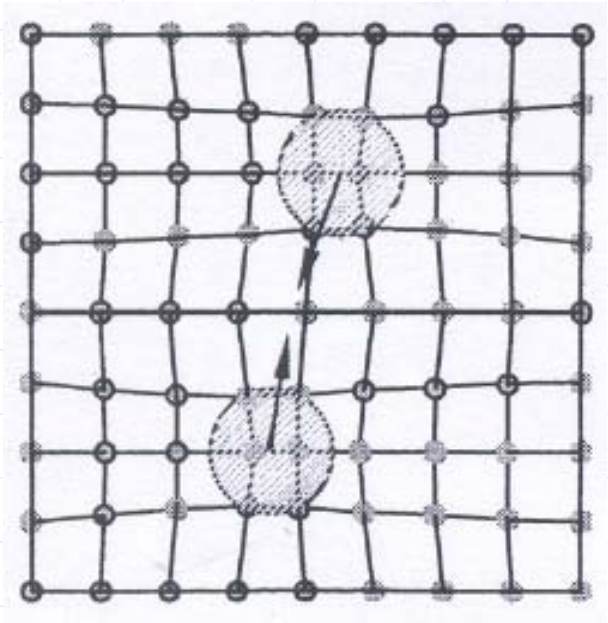
金属 Li

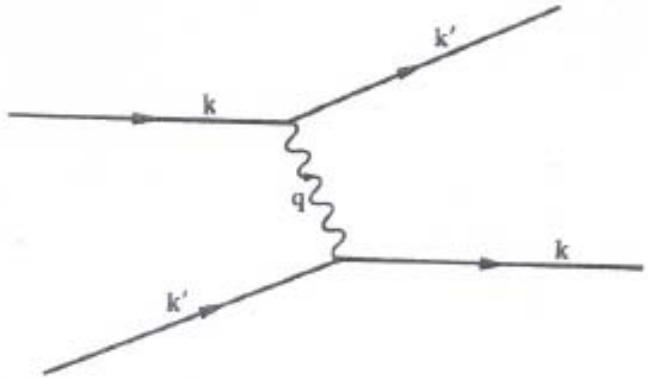


1. 共价键晶体中的电子是局域的

2. 处在共振价键态中的电子是半局域的

Cooper 对和金属的超导电性

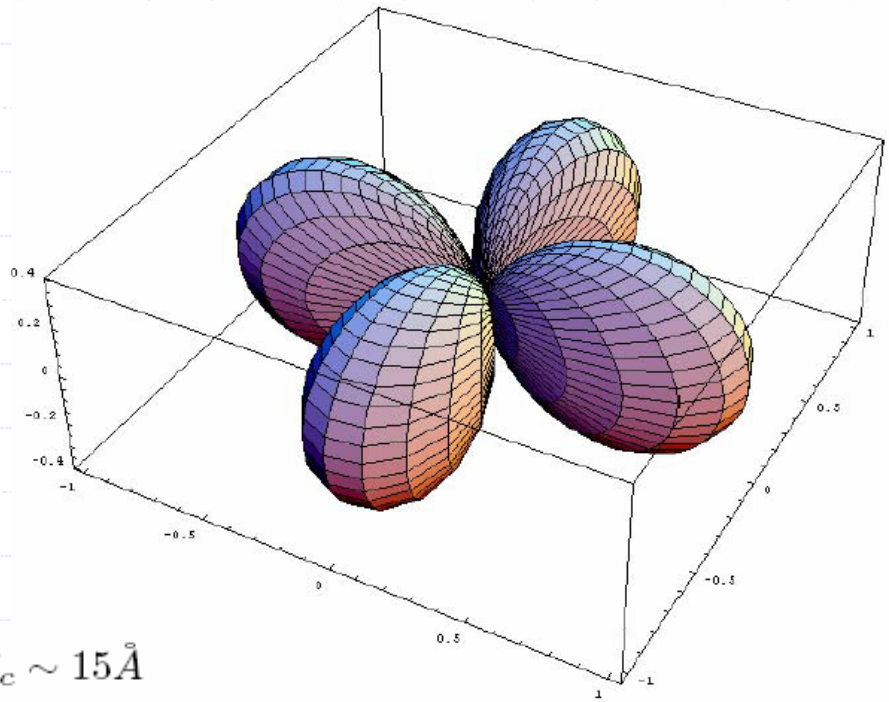




电－声相互作用是一种长程相互作用　　$\xi_c \sim 10^4 \mathring{A}$

超导态是一种量子凝聚状态，即有宏观数目的粒子占据了单一量子态。

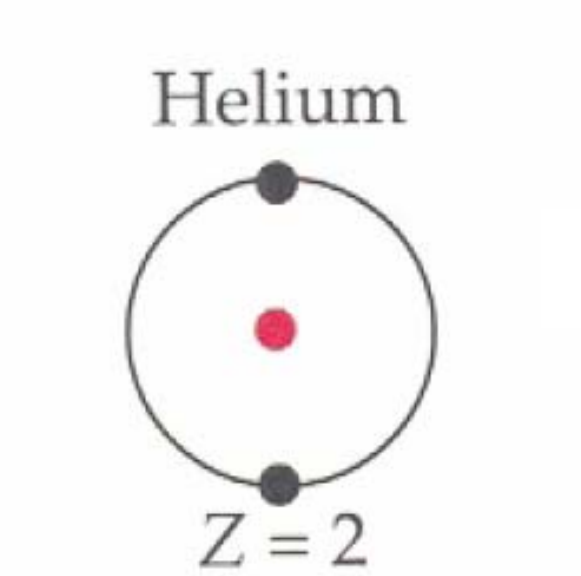
高温超导体中的电子对



电子相干长度 $\xi_c \sim 15\mathring{A}$

氦原子 - 交换积分 - Hund 定则

$$(H_1 + H_2 + V)\psi = E\psi$$



$$V = \frac{1}{4\pi\epsilon_0 r_{12}}$$

$$\psi = a u_{1s}(1)u_{nl}(2) + b u_{1s}(2)u_{nl}(1)$$

$$E = E_0 + \Delta E$$

$$\Delta E = J \pm K$$

$$a = b$$

$$a = -b.$$

$$J = \frac{1}{4\pi\epsilon_0}\int |u_{1s}(1)|^2 \frac{e^2}{r_{12}} |u_{nl}(2)|^2 d^3r_1 d^3r_2$$

$$K = \frac{1}{4\pi\epsilon_0}\int u^*_{1s}(1)u^*_{nl}(2)\frac{e^2}{r_{12}}u_{1s}(2)u_{nl}(1)d^3r_1 d^3r_2$$

对称和反对称波函数 - Hund 定则

$$\psi^S_{\text{space}} = \frac{1}{\sqrt{2}}\{u_{1s}(1)u_{nl}(2) + u_{1s}(2)u_{nl}(1)\}$$

$$\psi^A_{\text{space}} = \frac{1}{\sqrt{2}}\{u_{1s}(1)u_{nl}(2) - u_{1s}(2)u_{nl}(1)\}$$

$$\psi = \psi_{\text{space}} \times \psi_{\text{spin}}$$

$\psi^S_{\text{space}} \times \psi^A_{\text{spin}}$

$\psi^A_{\text{space}} \times \psi^S_{\text{spin}}$

S=0

$$\psi^A_{\text{spin}} = \frac{1}{\sqrt{2}}[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2)]$$

S=1

$$\psi^S_{\text{spin}} = \begin{cases} \chi_\uparrow(1)\chi_\uparrow(2), & m_S = 1 \\ \frac{1}{\sqrt{2}}[\chi_\uparrow(1)\chi_\downarrow(2) + \chi_\downarrow(1)\chi_\uparrow(2)], & m_S = 0 \\ \chi_\downarrow(1)\chi_\downarrow(2), & m_S = -1 \end{cases}$$

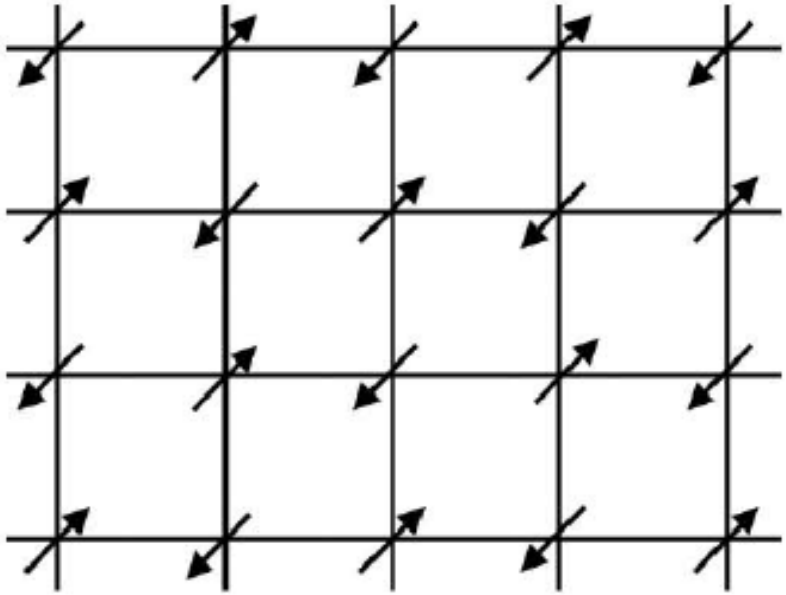
$$\Delta E = -K\mathbf{S_1} \cdot \mathbf{S_2}$$

格点自旋

海森伯模型

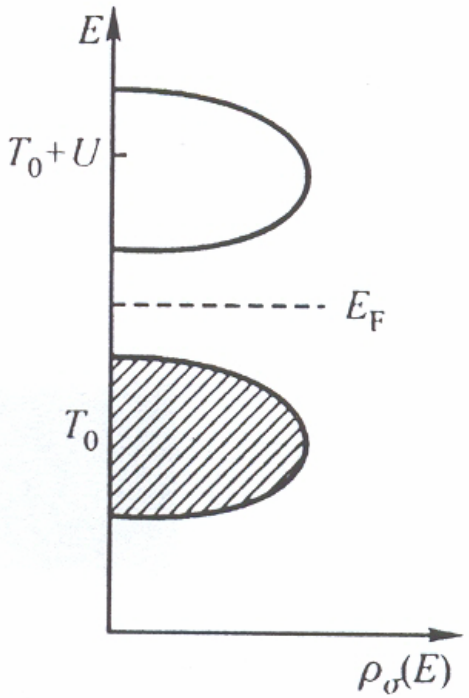
（局域电子模型）

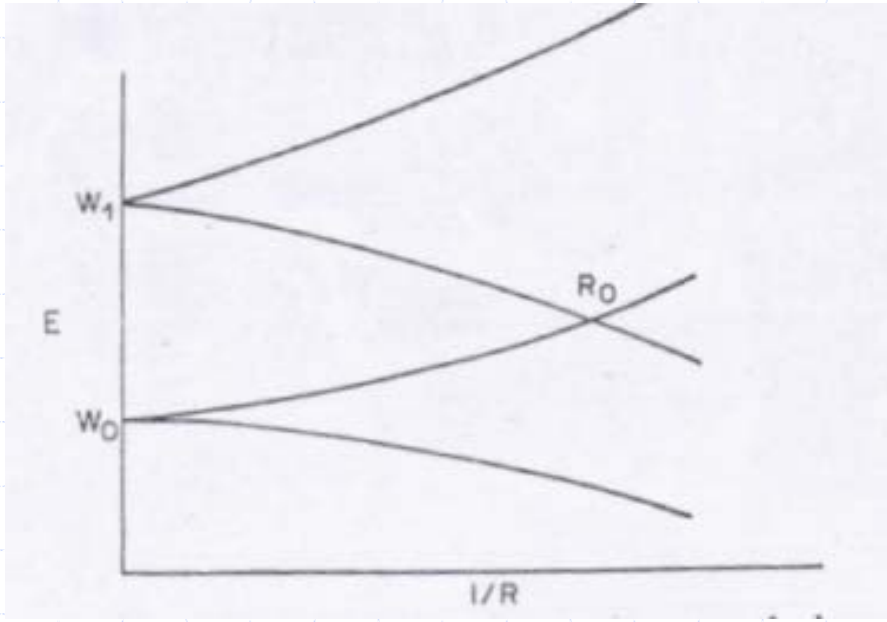
$$H = J \sum_{<i,j>} \mathbf{S_i} \cdot \mathbf{S_j}$$



莫特绝缘体（ Mott Insulator ）

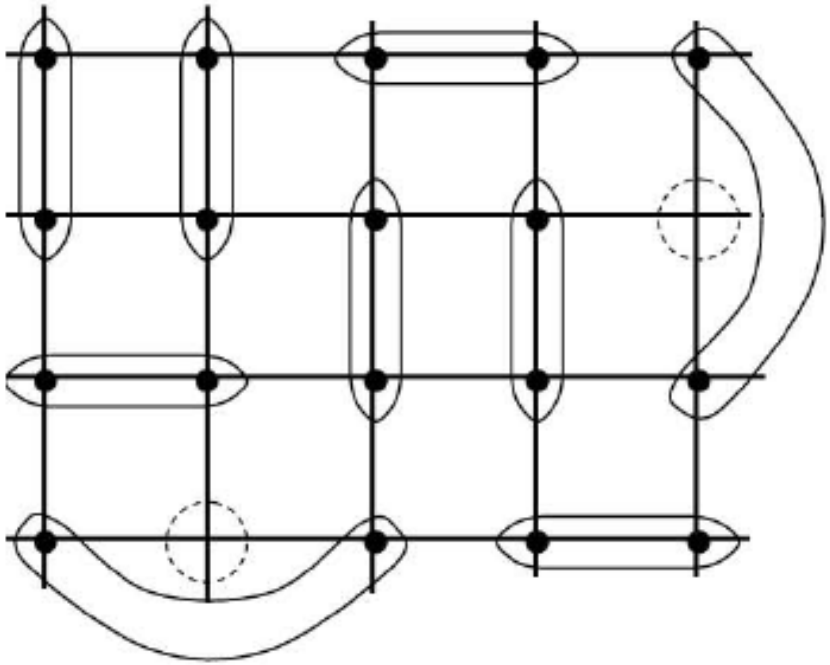
莫特绝缘体通常具有窄能带电子结构，其中在位库仑能不能忽略





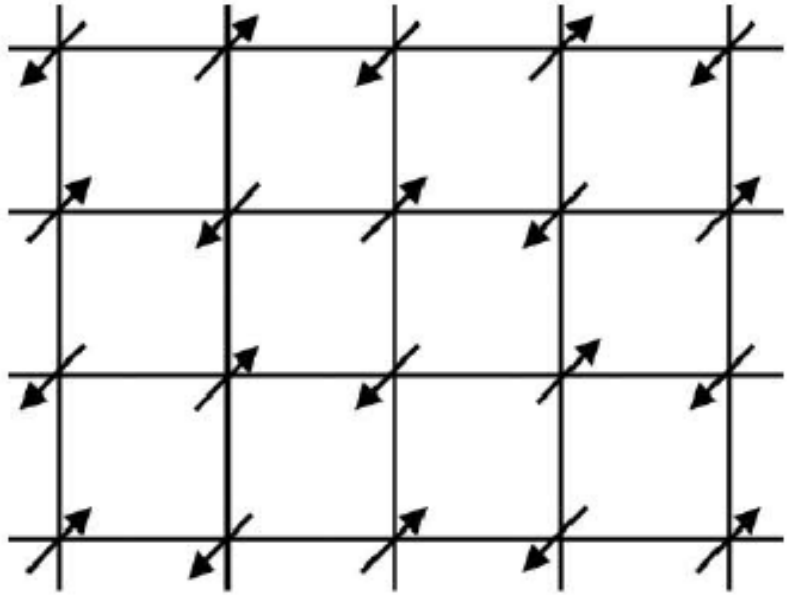
Anderson 的共振价键态理论

$$H = J \sum_{<i,j>} \mathbf{S_i} \cdot \mathbf{S_j}, \qquad S = 1/2$$



r  r' $= \dfrac{|\uparrow_r \downarrow_{r'}> - |\downarrow_r \uparrow_{r'}>}{\sqrt{2}}$

“自旋固体”



相邻自旋构成了自旋单态，称为 **自旋液体**

中子散射实验显示了铜位自旋的各向异性反铁磁有序

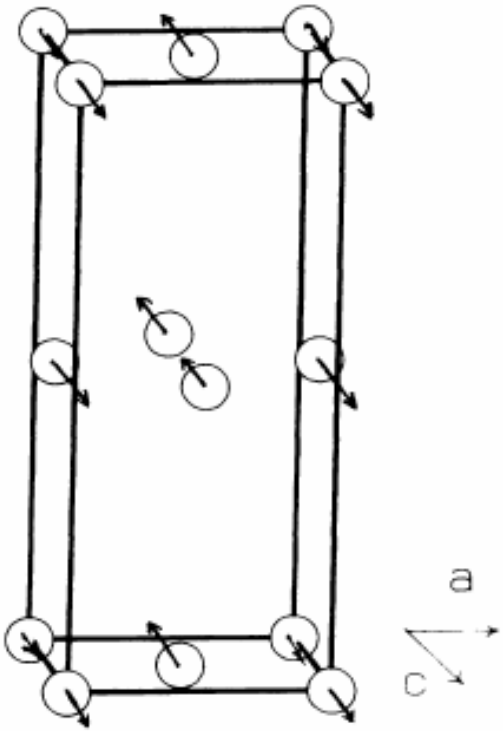
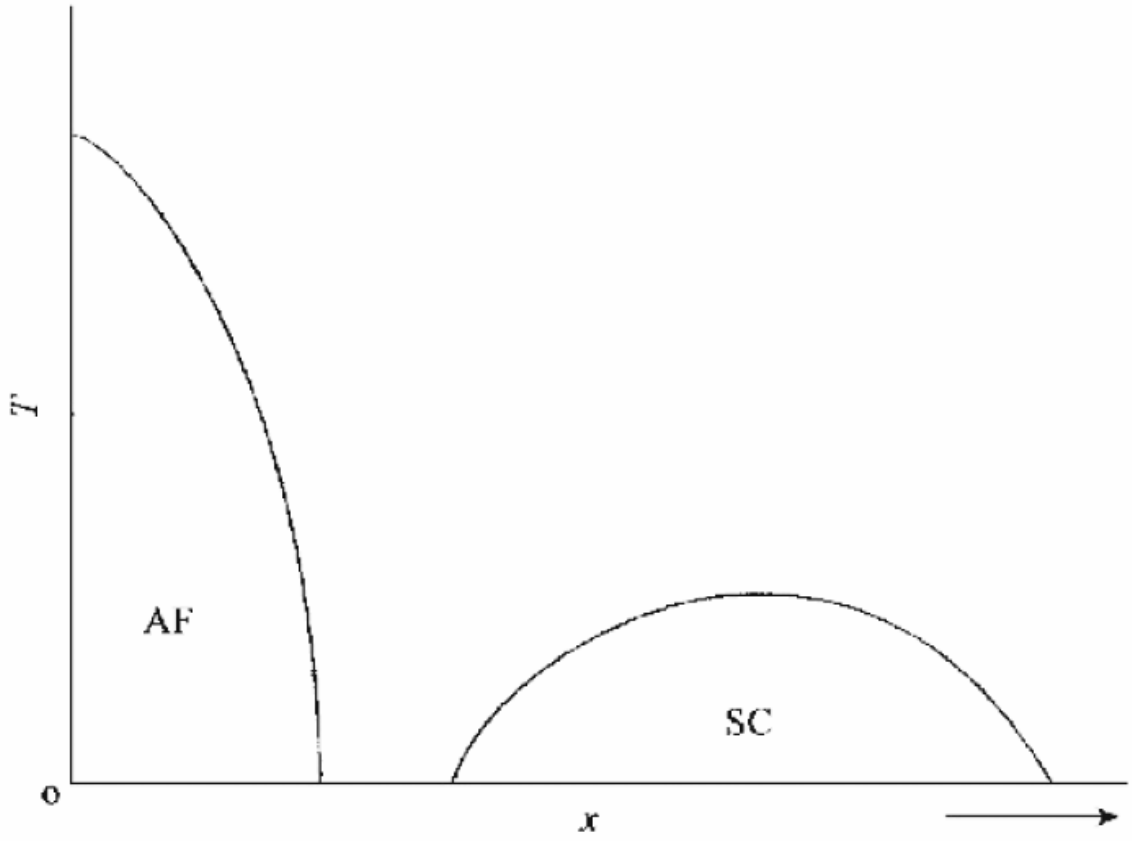


FIG. 3. Proposed spin structure of antiferromagnetic La_2CuO_{4-y}. Only copper sites in the orthorhombic unit cell are shown for clarity.

Vaknin D, et al. , 1987 Phys. Rev. Lett. **58** 2802

高温超导体的电子相图

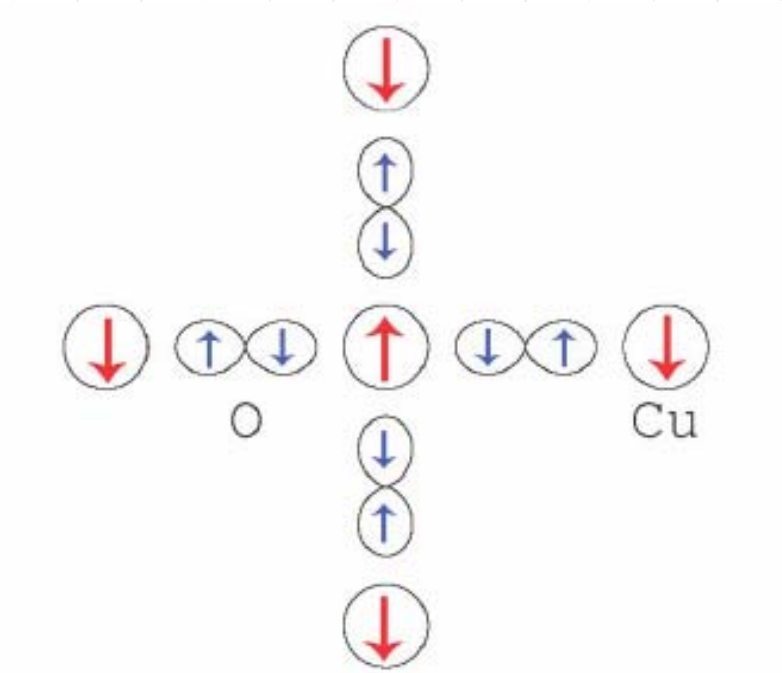


空穴掺杂浓度

随着空穴浓度的增加，反铁磁相向超导相的转化是

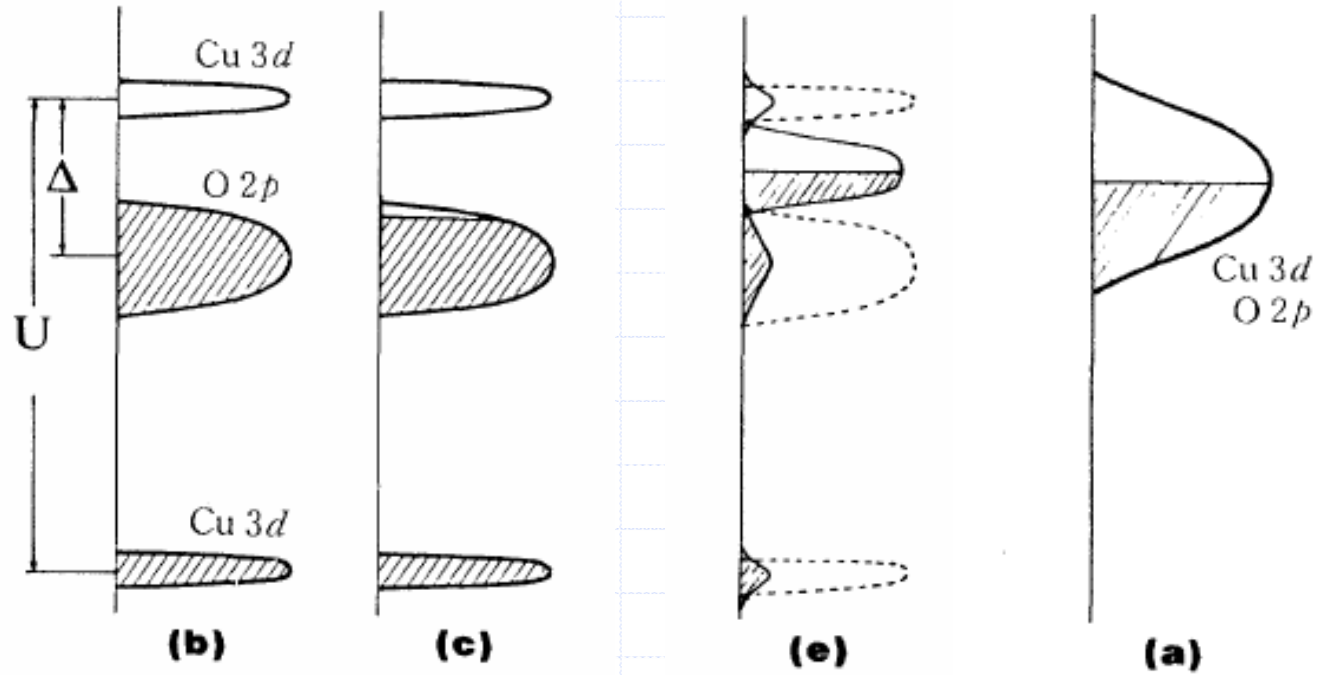
高温超导的核心问题

铜氧面的磁结构



铜位自旋的磁有序是通过氧位电子的媒介作用实现的。

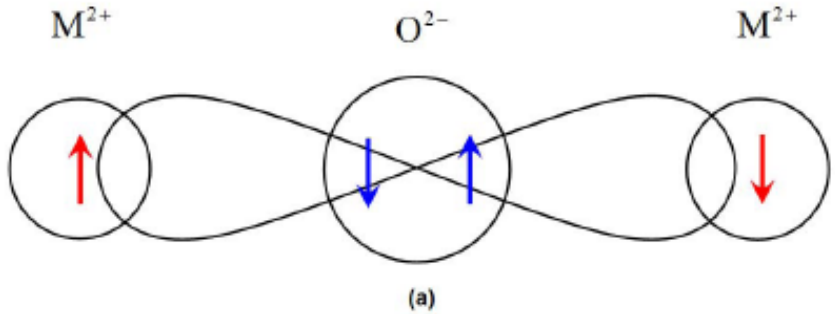
铜氧面电子结构随空穴掺杂的变化



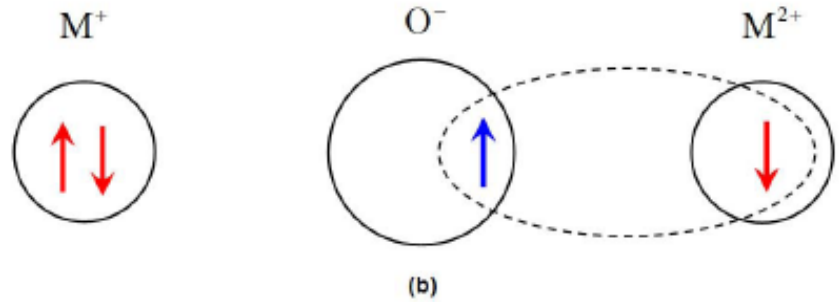
Uchida S, et al. 1991 Phys. Rev. B **43** 7942

超交换过程 – Kreamers 机制

基态



激发态



H. A. Kramer, Physica 1, 182(1934)

凝聚态磁性物理，姜寿亭等，科学出版社， 2003

超交换理论

二级微扰理论

$$H = H_0 + H'$$

$$E_0^{(2)} = \sum_m \frac{\langle 0|H'|m\rangle\langle m|H'|0\rangle}{E_0 - E_m}$$

有效哈密顿量

$$H' = H'(\hat{A}, \hat{B})$$

$$\tilde{H}(\hat{A}) = \sum_m \frac{\langle 0|H'|m\rangle_b\langle m|H'|0\rangle_b}{E_0 - E_m}$$

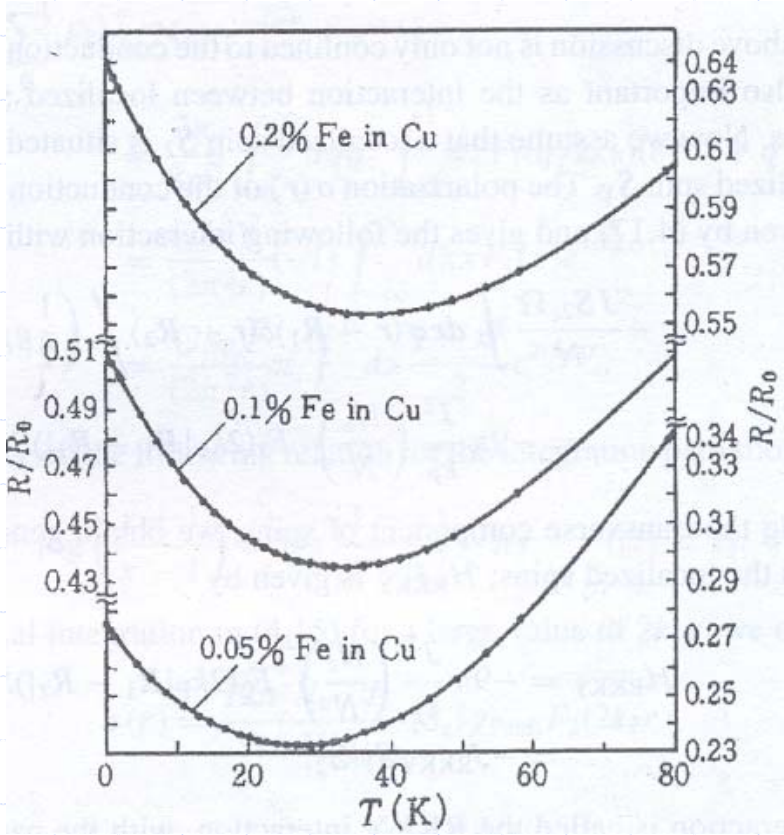
我们把氧位电子的自由度积掉便可以得到铜位自旋间的有效交换作用

共振态－近藤（Kondo）问题－s-d 交换模型

$$H = -J\mathbf{S}\cdot\sigma$$

S：局域自旋

σ: 传导电子自旋



传导电子和局域电子之间的自旋散射导致电阻极小。

$$R_s \propto \ln T$$

近藤（ Kondo ）问题 – s-d 交换模型

$$H = -J\mathbf{S}\cdot\sigma$$

S：局域自旋

σ: 传导电子自旋

求解 s-d 交换模型的基态

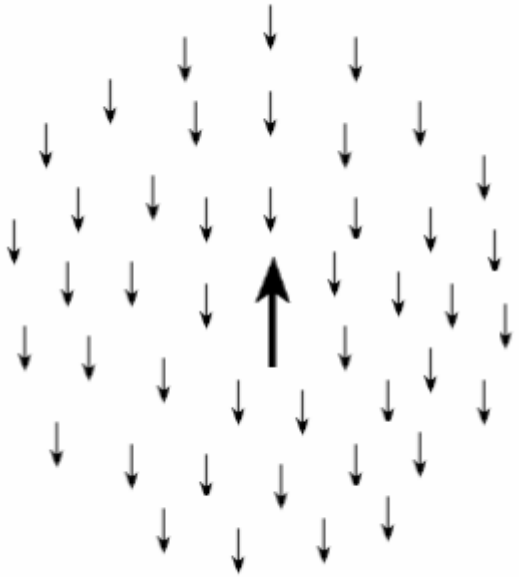
$$H|\psi\rangle = E|\psi\rangle$$

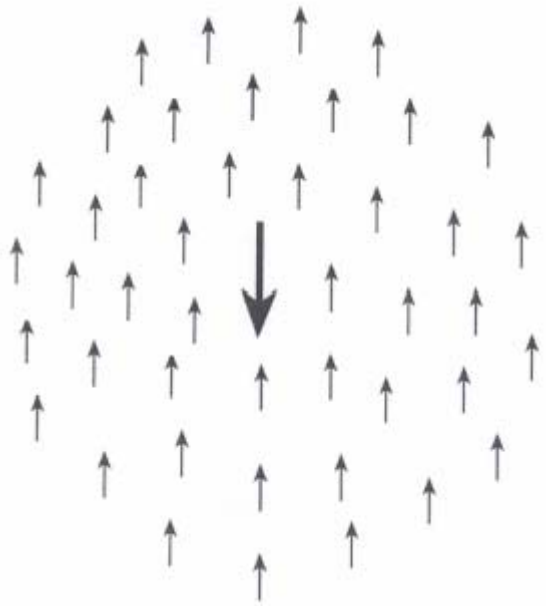
Yosida 波函数

$$|\psi\rangle = \sum_{k>k_F}[(\Gamma^{\alpha}_{k\uparrow}c^{\dagger}_{k\uparrow} + \Gamma^{\alpha}_{k\downarrow}c^{\dagger}_{k\downarrow})\chi_{\uparrow} + (\Gamma^{\beta}_{k\uparrow}c^{\dagger}_{k\uparrow} + \Gamma^{\beta}_{k\downarrow}c^{\dagger}_{k\downarrow})\chi_{\downarrow}]|F\rangle$$

基态波函数 $|\psi\rangle$ 为局域自旋和传导电子自旋构成的自旋单态

Kondo 单态是一种局域的电子共振态





S=0

传导电子自旋屏蔽了局域自旋，形成非磁的基态

小结

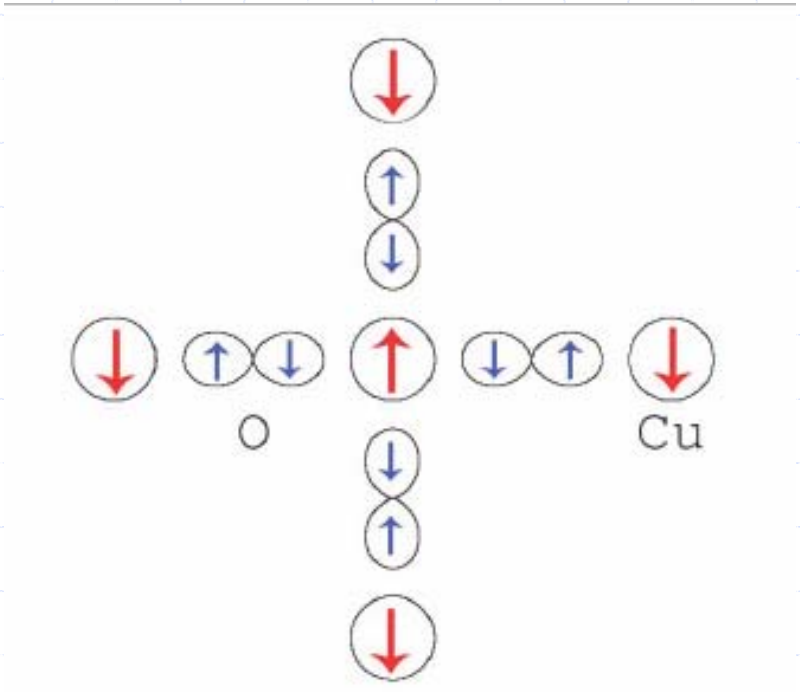
1. 氢分子 (共价键，局域电子，交换作用)

2. Cooper 对（巡游电子，电 – 声相互作用）

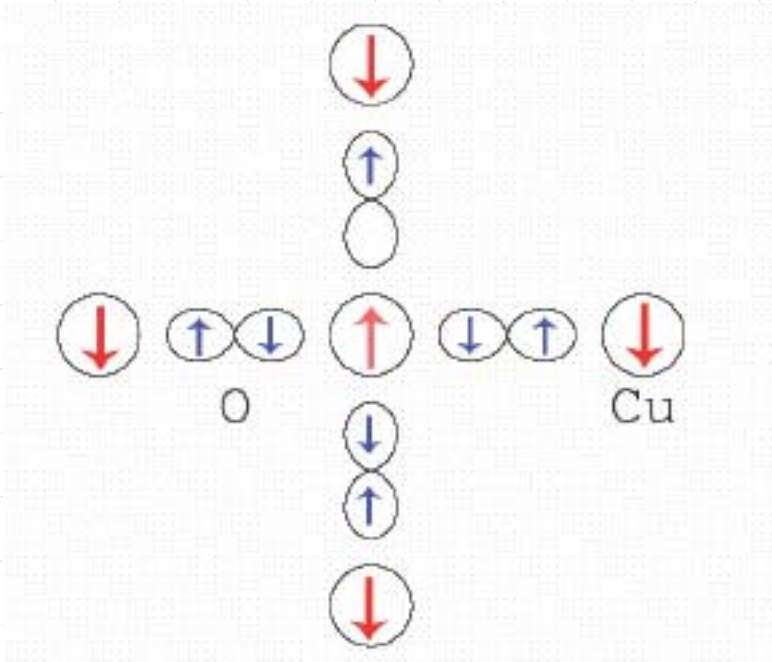
3. Kondo 自旋单态（巡游电子和局域电子形成的局域共振态，交换作用）

4. RVB 态，幻想还是现实？

铜氧面磁结构随掺杂的变化

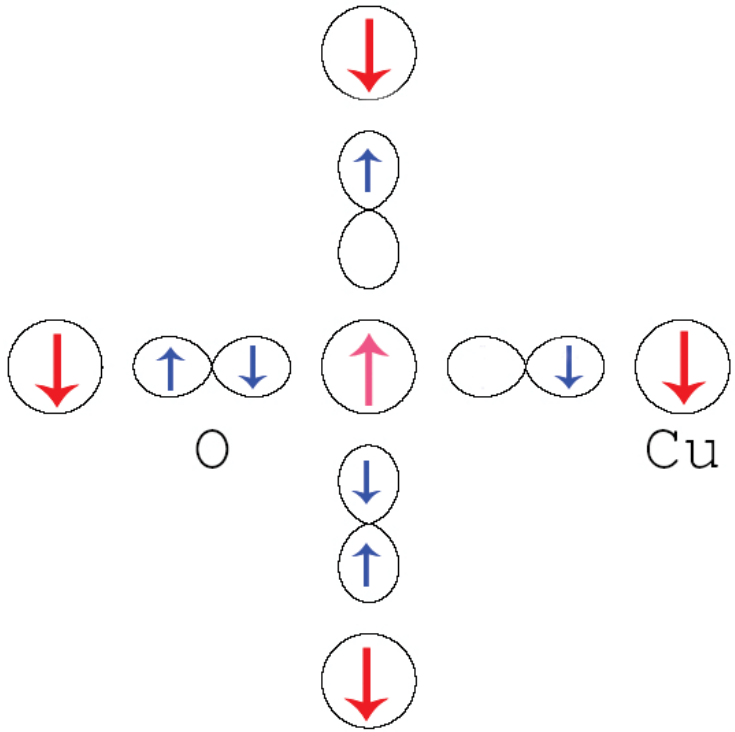


零掺杂



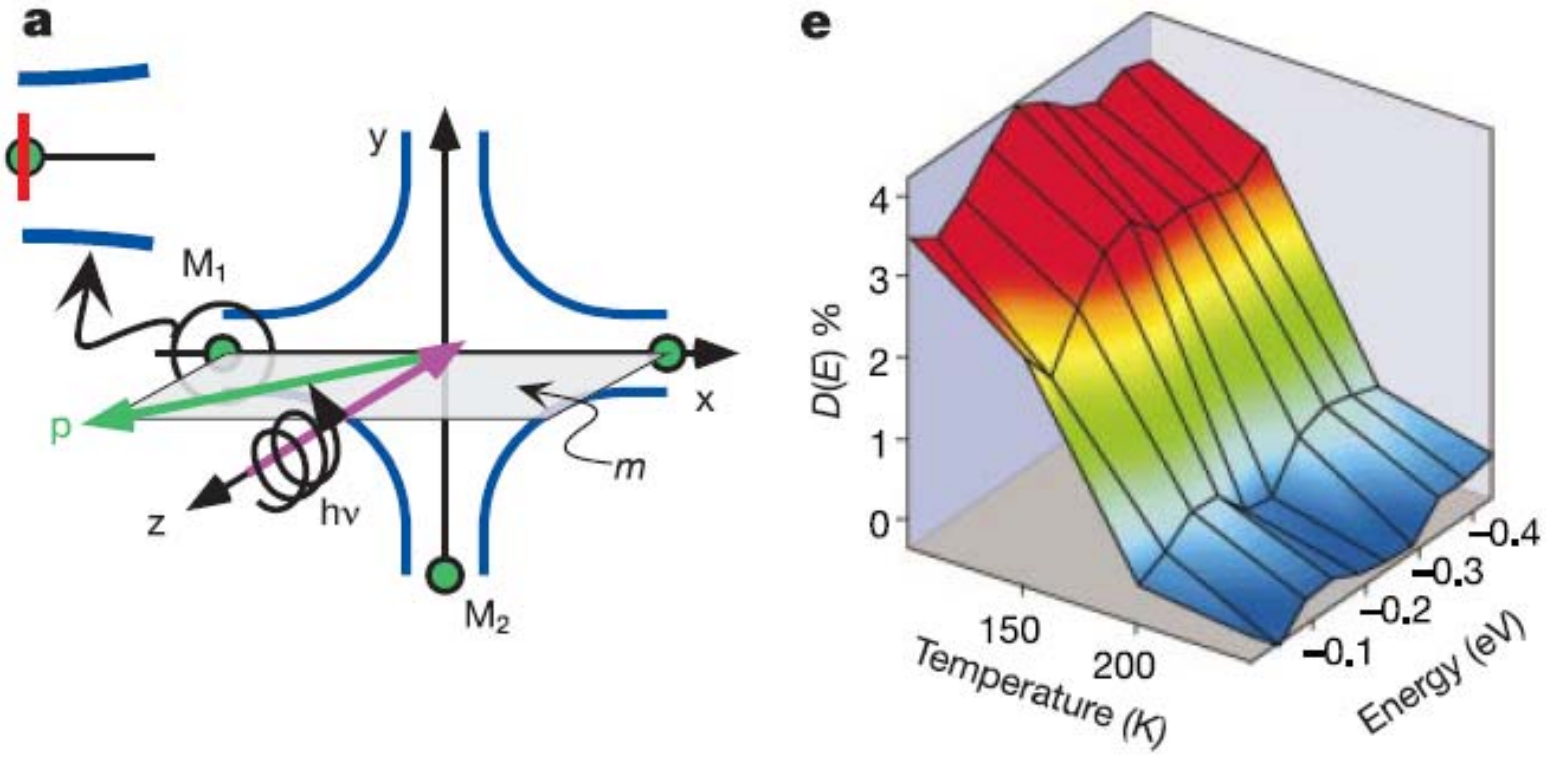
掺杂空穴出现在氧位上，导致铜位电子超交换的弱化

因空穴掺杂产生的氧位失配自旋是否可以形成 RVB ？



超导载流子浓度正比于掺杂浓度 $n_s \propto x$

Time reversal symmetry breaking effect observed in circular polarized photoemission experiement



A. Kaminski *et al.* , Nature **416** , 610(2002)

两个氧位电子自旋和邻近的铜位自旋之间的相互作用

$$H_m = K \sum_{<ij>} S_i S_j, \qquad K \sim \rho^2 J_d \qquad \rho = \int d^3x \phi_d^*(\mathbf{x}) V_{mix} \phi_p(\mathbf{x})$$

$$\hat{H}_{\rm int} = -J\mathbf{S_0} \cdot (\sigma_1 + \sigma_2) \quad (J < 0)$$

二级微扰理论

$$\delta E = \langle 0|\hat{H}_{\rm int}|0\rangle + \frac{\langle 0|\hat{H}_{\rm int}|1\rangle\langle 1|\hat{H}_{\rm int}|0\rangle}{E_0 - E_1}$$

两个氧位自旋之间的有效相互作用

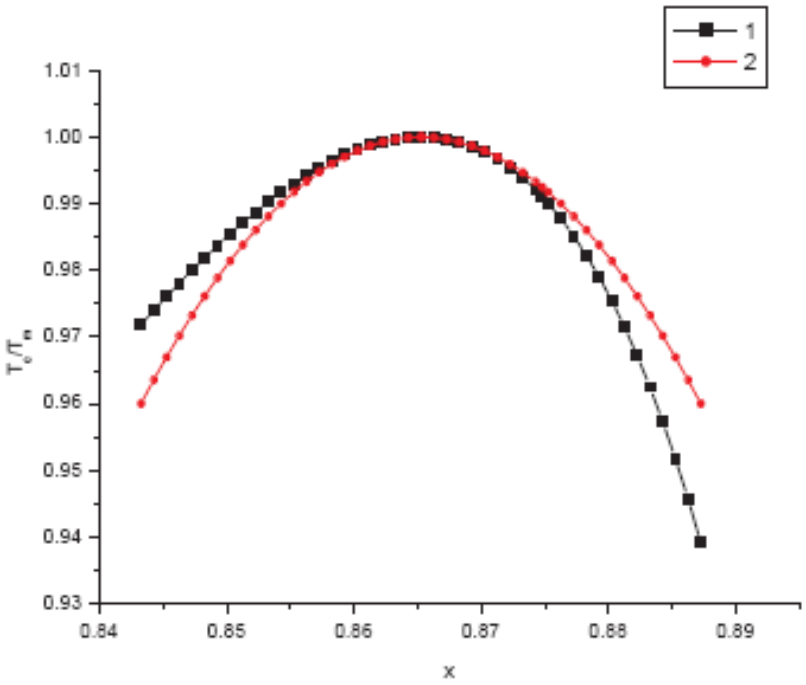
$$H_{eff} = -\frac{1}{4}\lambda J(\sigma_1^+ + \sigma_2^+)(\sigma_1^- + \sigma_2^-), \qquad \lambda = J/4K$$

$$K = K_0(1-y)$$

本征函数 $$\chi_+ = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

束缚能 $E_b = -\frac{1}{2}\lambda J(1-\frac{1}{2}\lambda^2)$

$\lambda_{max}^2 = \frac{2}{3}$



$\frac{T_c}{T_m} = \frac{E_b}{E_m}$

$T_c/T_m = 1-\kappa(x-x_0)^2,$

$\kappa = (4K_0/J)^2$

$\kappa = 82.6,\ x_0 = 0.16.$

$K_0/|J| = 2.27.$

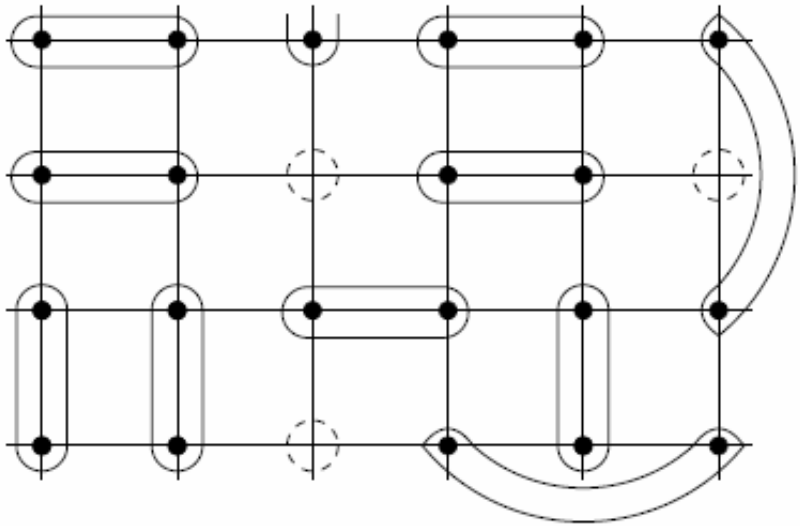
$T_{max} = \frac{1}{3k_B}\cdot\lambda_{max}J$ $\qquad K_0 = 0.1\text{eV}, \quad T_c \approx 150\text{K}$

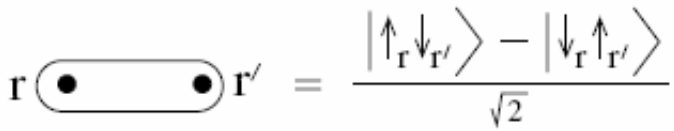
高温超导转变温度上限和最佳掺杂浓度唯一由母化合物的超交换强度 K_0 所决定

The single band RVB theory

P W Anderson *et al.* J. Phys.: Condens. Matter **16** (2004) R755–R769

$$H_{t-J} = PTP + J\sum_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$





Knight 位移测量提供了铜氧面超导态的关键信息：

- 电子结构
- 自旋状态
- d 波对称

核磁共振和 Knight 位移

核自旋周围的电子磁矩对共振频率有影响

频移 $\Delta\omega_N = \gamma_N \langle \delta H \rangle$

Knight 位移定义为 $K = \langle \delta H \rangle / H_0$

$$K = K_s + K_l$$

$$\delta H_l = \mu_B \langle l_z \rangle = \chi_l H_0$$

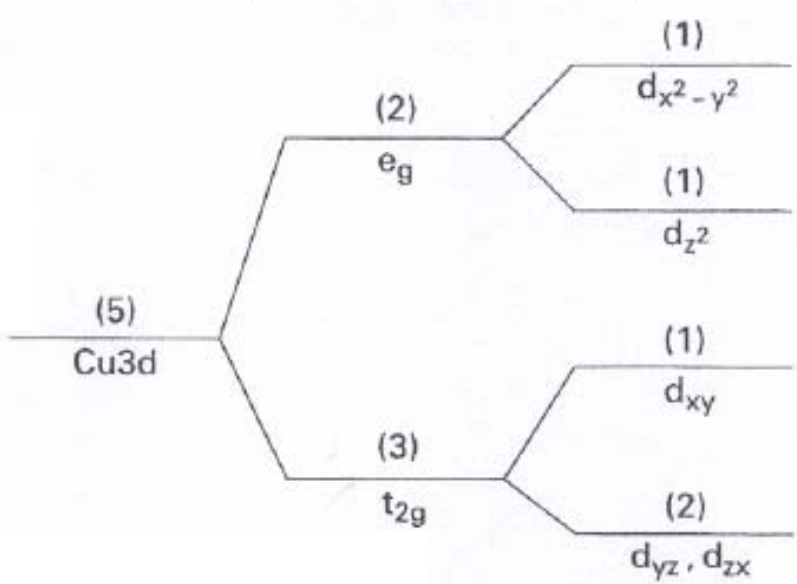
$$\delta H_s = 2\mu_B \langle s_z \rangle = \chi_s H_0$$

χ_l: 轨道磁化率 χ_s: 自旋磁化率

处于 Cu^{2+} 离子轨道中的电子能级在晶场中的劈裂

轨道磁化率

$$\chi_{orb} = 2\mu_B^2 \sum_n \frac{|\langle n | \hat{L} | x^2 - y^2 \rangle|^2}{E_n - E_{x^2-y^2}}$$



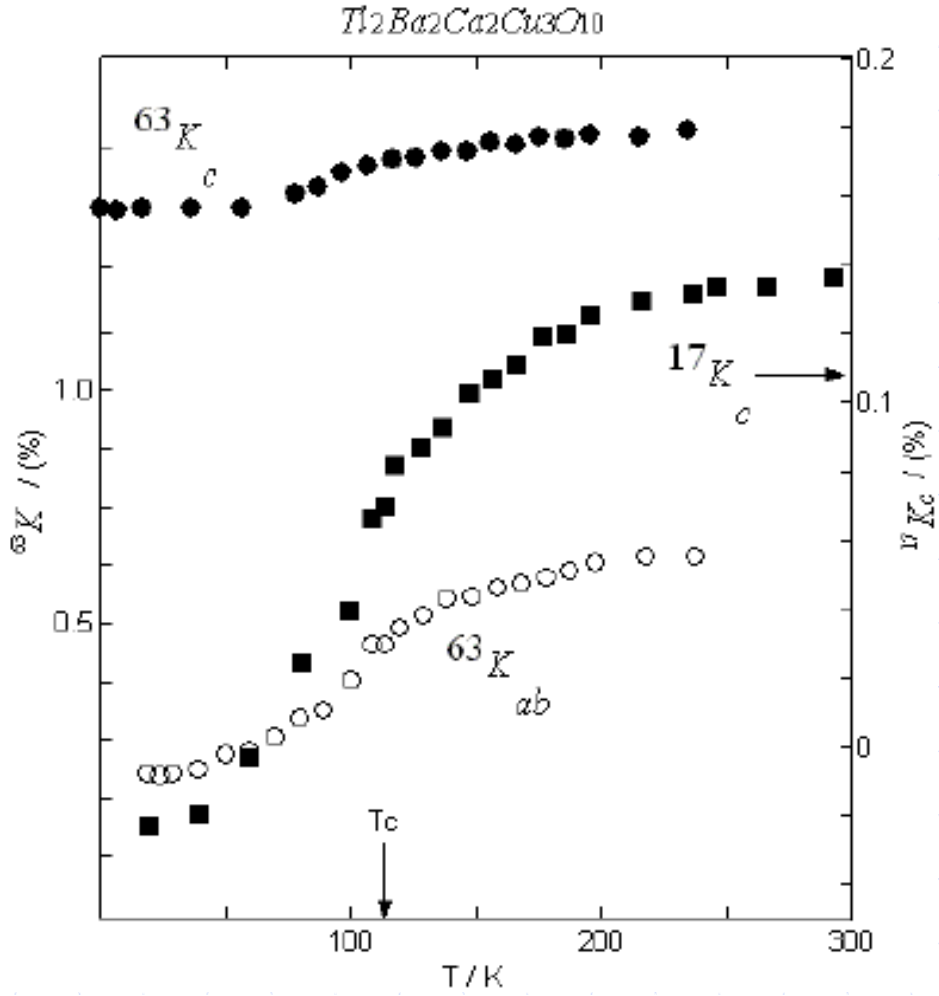
磁场沿 c 轴和 ab 轴方向的 $d_{x^2-y^2}$ 轨道磁化率之比为 4

$$\frac{\chi_{orb}^{c}}{\chi_{orb}^{ab}} \approx 4$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^{+2} + Y_2^{-2})$$

Mila F, Rice T M, 1989 Physica C **157** 561

铜氧面 Knight 位移测量数据



郑国庆，”高温超导基础研究”，上海科学出版社， p348

Zheng G Q, et al., 1996 Physica **C 260** , 197

JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS VOLUME 88, NUMBER 3 MARCH 1999

Features of the spin fluctuations and superconductivity of $Tl_2Ba_2CaCu_2O_{8-\delta}$ according to ^{63}Cu and ^{17}O NMR data

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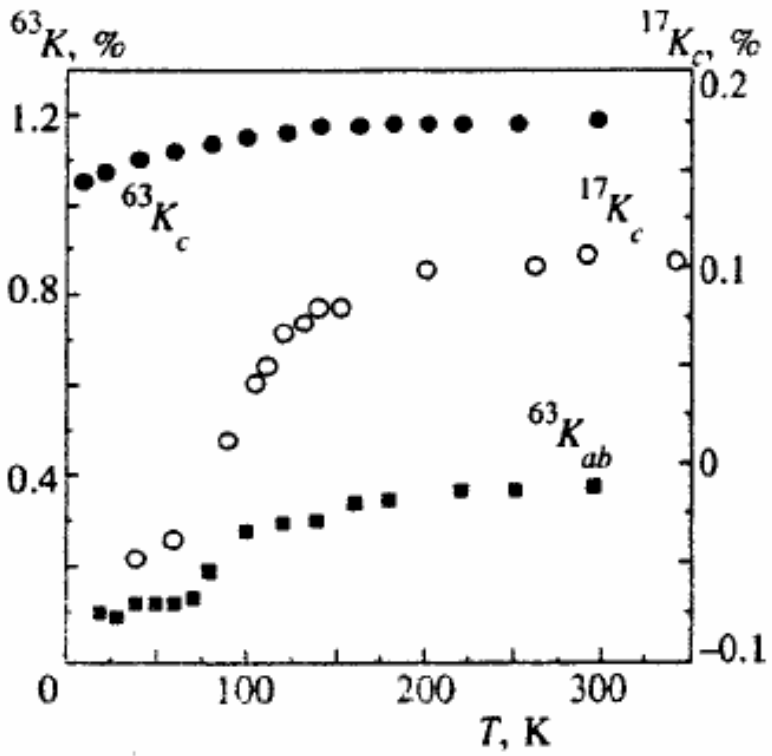
(Submitted 18 November 1998)
Zh. Éksp. Teor. Fiz. **115**, 991–1001 (March

Data on the NMR line shifts, the spin–lattic
spin–spin relaxation rate of ^{63}Cu are obtain
and superconducting states. The hyperfine c
CuO_2 plane are estimated from an analysis
The temperature-dependent behavior of the
dynamic spin susceptibility is discussed by
possible relation between the characteristics
superconducting transition temperature is an
Institute of Physics. [S1063-7761(99)01603-

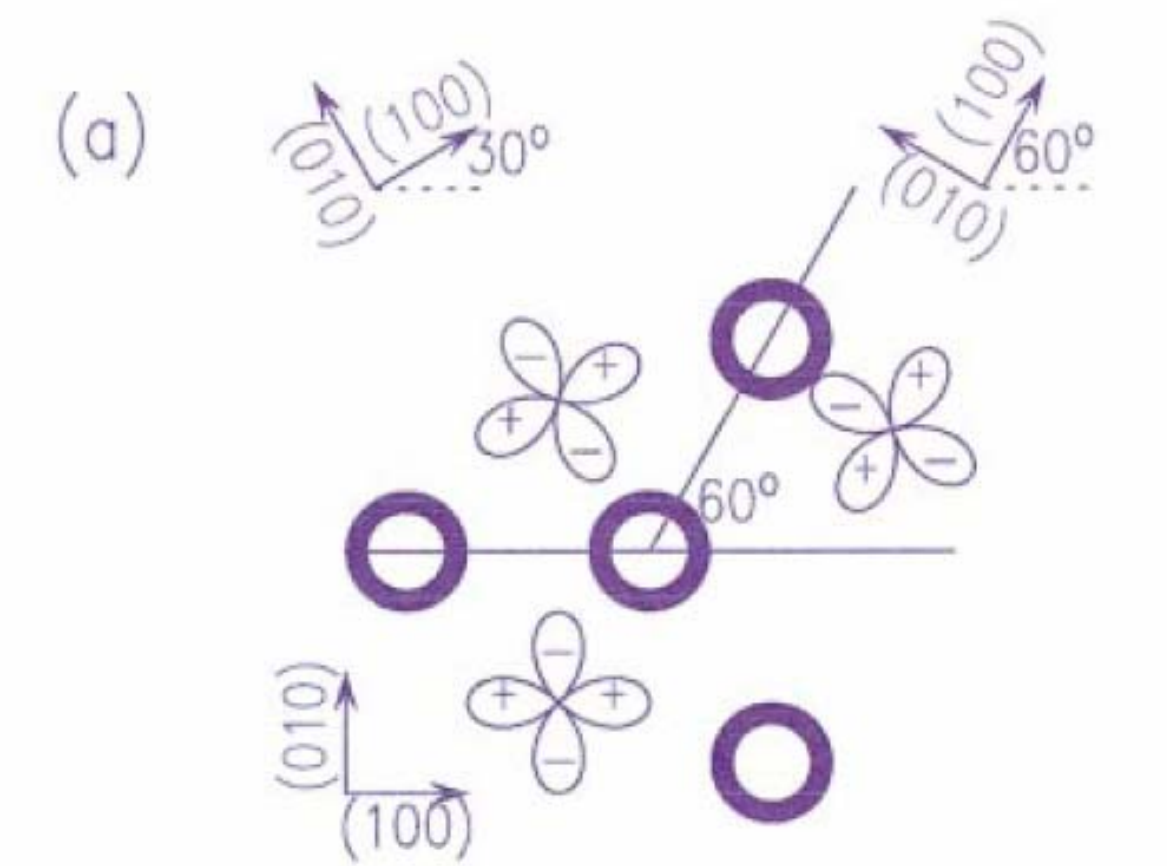


1. INTRODUCTION

Studies of high-T_c superconductivity carried out
the past 10 years have revealed some special features

d 波对称的实验观察

Tsuei C C, Kirtley J R, 2000 Rev. Mod. Phys. **72** , 969



电子对波函数

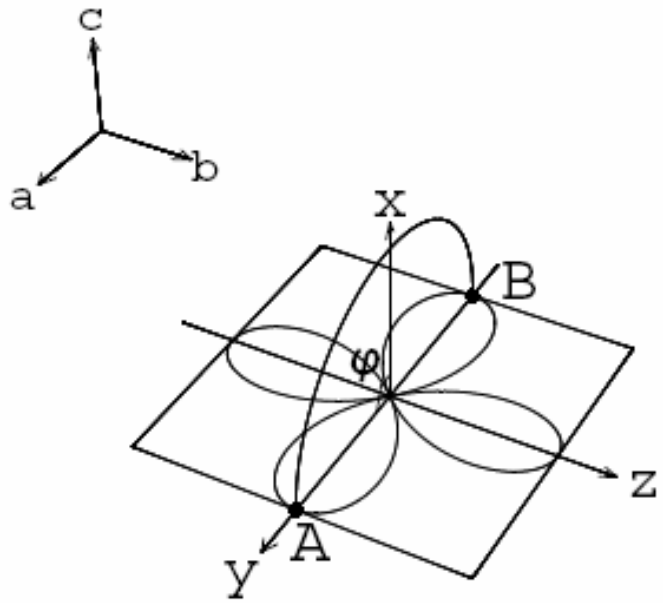
$$\psi_d = Y_2^{+1}(\theta_1,\varphi_1)Y_2^{-1}(\theta_2,\varphi_2) - Y_2^{-1}(\theta_1,\varphi_1)Y_2^{+1}(\theta_2,\varphi_2)$$

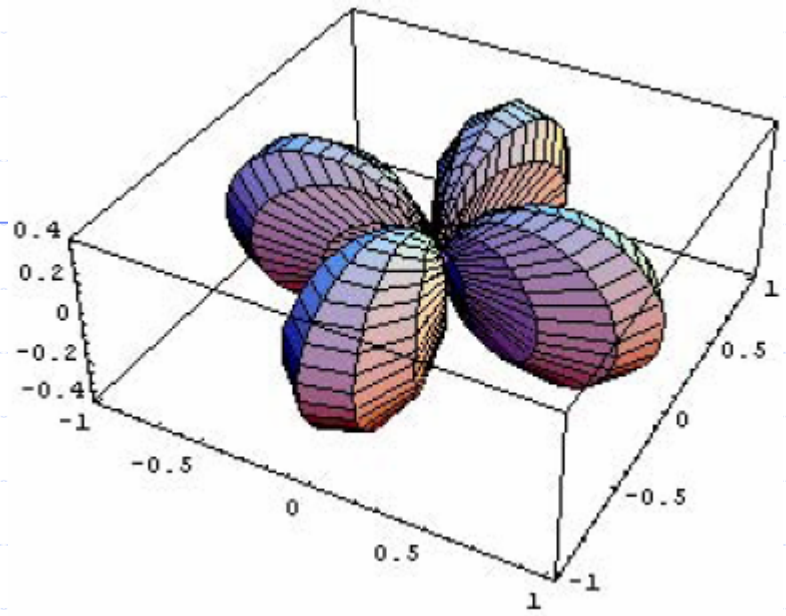
磁量子数：

$$M = m_1 + m_2 = 0$$

$$\psi_d \propto \cos 2\theta \ \sin\varphi$$

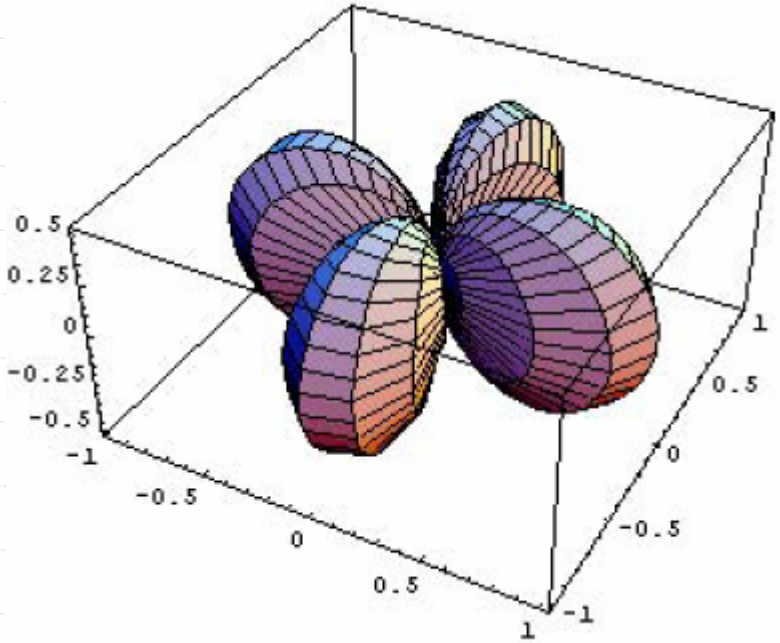
$$\theta = \theta_1 - \theta_2\ , \quad \varphi = \varphi_1 - \varphi_2.$$





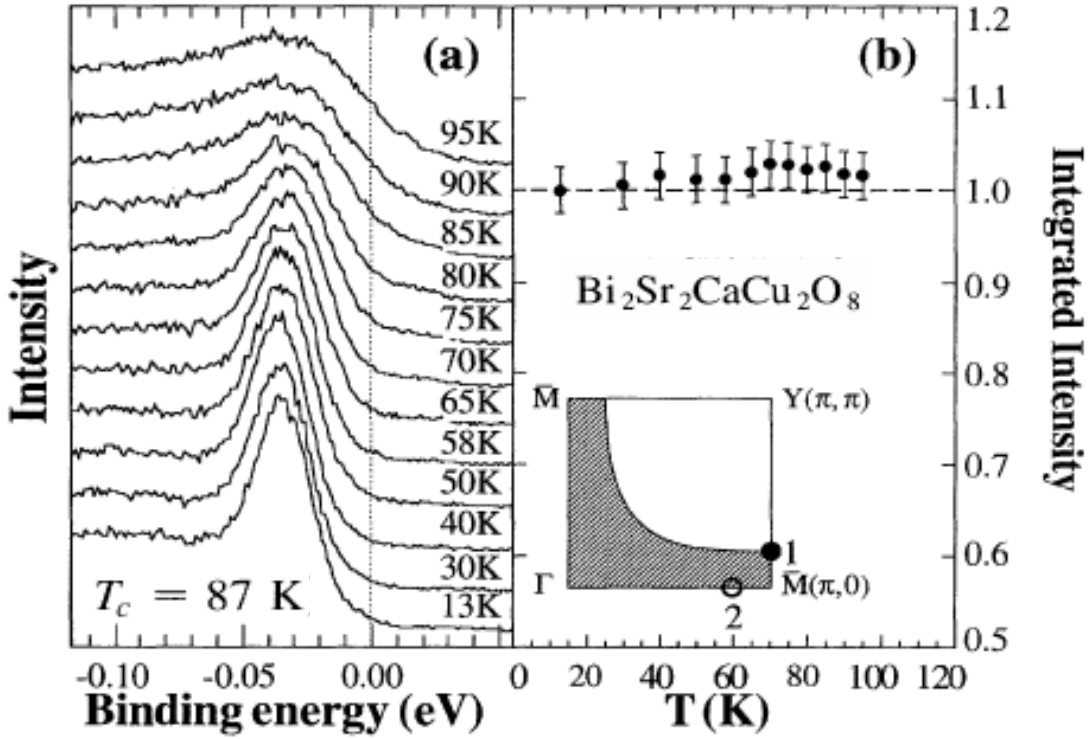
$d_{x^2-y^2}$

ψ_d



赝能隙是高温超导体的基本属性之一，

它是电子局域配对所导致的



结论

- 超导态下，铜氧面具有两分量结构（ 由 **p** 和 **d** 电子 构成）
- 氧位 电子自旋形成了 **RVB** 态
- **d** 波对称 源于反对称波函数

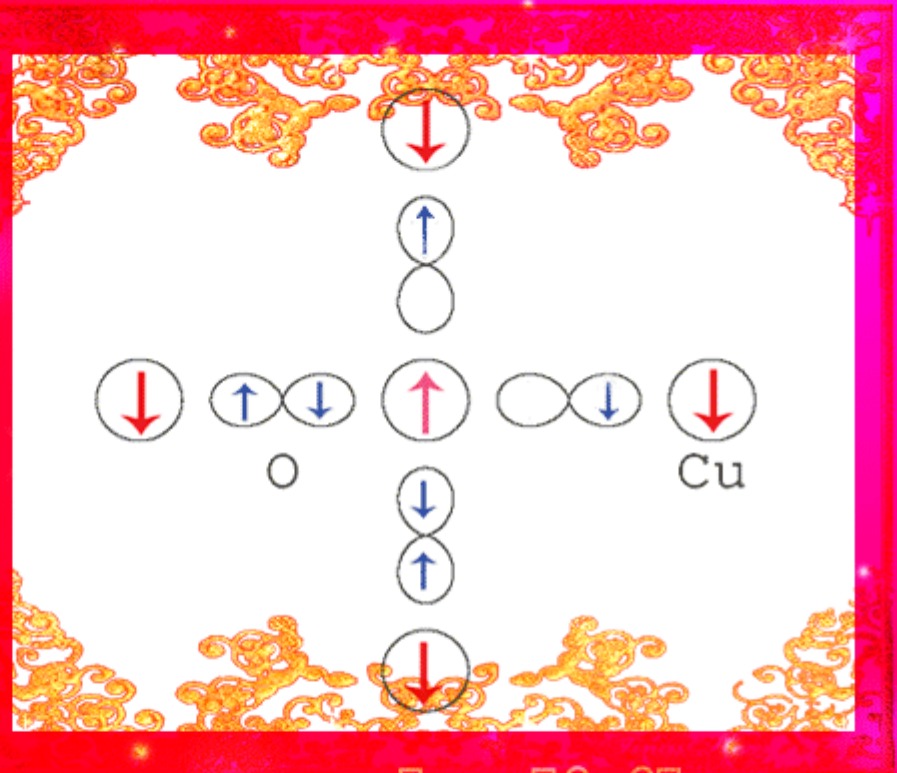
恭贺新年

magnetism

super

exchange

RVB



superconductivity

1957

K-J model

2007

吉祥如意