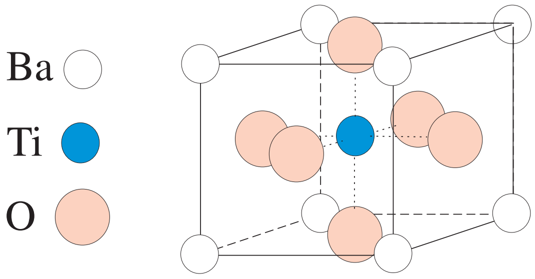
Solution to the MID TERM - SOLID STATE PHYSICS 2019

Problem 3



Unit cell of $BaTiO_3$

The X-ray structure factor is given by

$$S_{(hkl)} = \sum_d f_d e^{i\mathbf{k}_{(hkl)}\cdot\mathbf{R}_d} = \sum_d f_d e^{2\pi i(hx_d+ky_d+lz_d)}$$

where $\mathbf{R}_d = (x_d, y_d, z_d)$ are the positions of atom d in the unit cell, and f_d it the corresponding form factor (which we take to be proportional to Z_d). If we are interested in $(00l)$ we set $h = k = 0$ and obtain

$$S_{(00l)} = f_{Ba} + (-1)^l f_{Ti} + [1 + 2(-1)^l]f_O$$

The Bragg peak intensity is proportional to the square of the structure factor (times a multiplicity factor, but the multiplicity for all (001) are the same!), thus we obtain

$$\frac{I_{002}}{I_{001}} = \frac{(f_{Ba} + f_{Ti} + 3f_O)^2}{(f_Ba - f_{Ti} - f_O)^2} \approx 15.4$$

In reality the form factor depends on the scattering vector, and the variation is different from each atom, so this is just an approximation.

Problem 2.

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1) Each of the MOs is a linear combination of 6 pz orbitals

$$\psi^{\mu} = \sum_{i=1}^{6} c_i^{\mu} p_z^i \qquad \rightarrow \qquad \mathbf{c}^{\mu} = \begin{pmatrix} c_1^{\mu} \\ c_2^{\mu} \\ c_3^{\mu} \\ c_4^{\mu} \\ c_5^{\mu} \\ c_6^{\mu} \end{pmatrix}$$

2) It is relatively easy to work out the Hamiltonian. It is a 6-by-6 matrix. The first rule implies that every diagonal element is α:

$$\mathbf{H} = \begin{pmatrix} \alpha & & & & & \\ & \alpha & & & & \\ & & \alpha & & & \\ & & & \alpha & & \\ & & & & \alpha & \\ & & & & & \alpha \end{pmatrix}$$

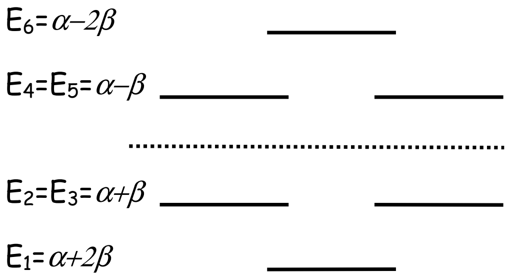
The only other non-zero terms will be between neighbors: 1-2, 2-3, 3-4, 4-5, 5-6 and 6-1. All these elements are equal to β:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix}$$

All the rest of the elements involve non-nearest neighbors and so are zero:

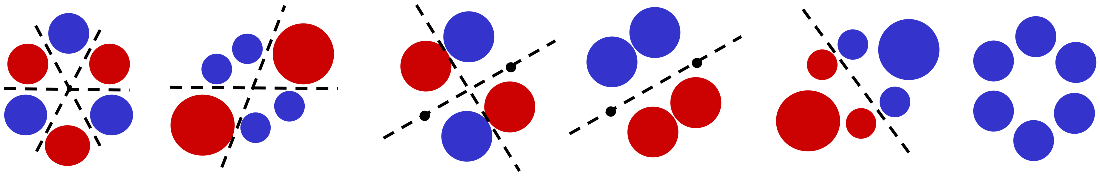
$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

3) Finding the eigenvalues of **H** is easy with a computer. We find 4 distinct energies:



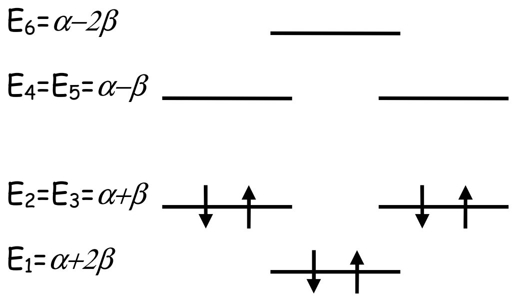
The lowest and highest energies are non-degenerate. The second/third and fourth/fifth energies are degenerate with one another. With a little more work we can get the eigenvectors. They are:

$$\mathbf{c}^6=\frac{1}{\sqrt{6}}\begin{pmatrix}+1\\-1\\+1\\-1\\+1\\-1\end{pmatrix}\quad \mathbf{c}^5=\frac{1}{\sqrt{12}}\begin{pmatrix}+1\\-2\\+1\\+1\\-2\\+1\end{pmatrix}\quad \mathbf{c}^4=\frac{1}{\sqrt{4}}\begin{pmatrix}+1\\0\\-1\\+1\\0\\-1\end{pmatrix}\quad \mathbf{c}^3=\frac{1}{\sqrt{4}}\begin{pmatrix}+1\\0\\-1\\-1\\0\\+1\end{pmatrix}\quad \mathbf{c}^2=\frac{1}{\sqrt{12}}\begin{pmatrix}+1\\+2\\+1\\-1\\-2\\-1\end{pmatrix}\quad \mathbf{c}^1=\frac{1}{\sqrt{6}}\begin{pmatrix}+1\\+1\\+1\\+1\\+1\\+1\end{pmatrix}$$



The pictures at the bottom illustrate the MOs by denting positive (negative) lobes by circles whose size corresponds to the weight of that particular p_z orbital in the MO. The resulting phase pattern is very reminiscent of a particle on a ring, where we saw that the ground state had no nodes, the first and second excited states were degenerate (sine and cosine) and had one node, the third and fourth were degenerate with two nodes. The one difference is that, in benzene the fifth excited state is the only one with three nodes, and it is non-degenerate.

4) There are 6 π electrons in benzene, so we doubly occupy the first 3 MOs:



5) The Hückel energy of benzene is then:

$$E=2E_1+2E_2+2E_3=6\alpha+8\beta$$

Problem 1.

1. Like the body-centered cubic cell, the body-centered tetragonal cell has two Bravais lattice points per conventional cell. The latter contains twice the chemical formula La_2CuO_4 (see Fig. 1a). A possible primitive cell containing the formula La_2CuO_4 only once is shown in Fig. 1b. It is constructed from the vectors $a(-1,0,0)$, $a(0,1,0)$, and $(-a/2,a/2,c/2)$.

2. 2La and 4O give an even number of electrons per unit cell. However, copper has an odd number of electrons. The primitive cell thus contains an odd number of electrons. There will therefore be at least one partially occupied band in an LCAO calculation and this leads to a metallic state.

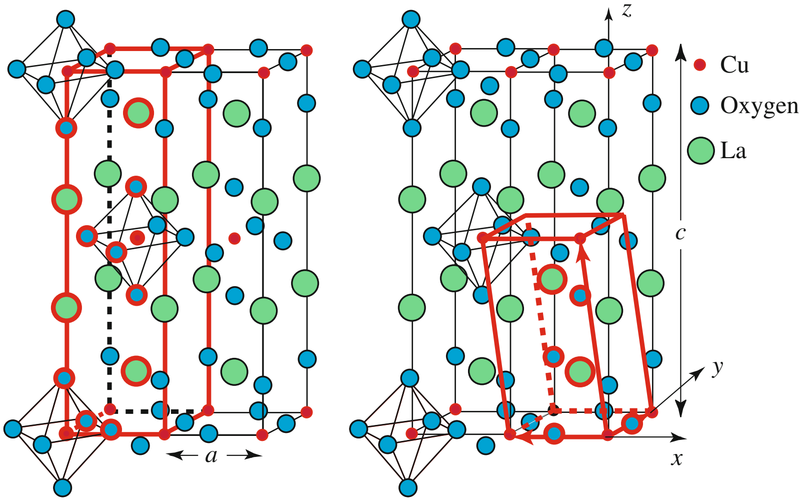
3. The square primitive cell in the CuO_2 plane containing one Cu atom and two O atoms is shown in Fig. 2a. The square reciprocal lattice of side $2\pi/a$ and the first Brillouin zone are depicted in Fig. 2b

4. The LCAO calculation gives $E(k_x,k_y) = E_0 - t_0 - 2t_1(\cos k_x a + \cos k_y a)$. The constant energy curves are

$$\cos k_x a + \cos k_y a = \frac{E_0 - t_0 - E}{2t_1}\,.$$

These are almost circular curves around $k = 0$ for $E \gtrsim E_0 - t_0 - 2t_1$ and around $k = (\pi/a, \pi/a)$ for $E \lesssim E_0 - t_0 + 2t_1$. For one electron per cell, the last filled level corresponds to a half-filled band, or

$$E = E_0 - t_0\,,$$



(a) (b)

Fig. 1 Crystal structure of La_2CuO_4. (**a**) Conventional cell containing twice La_2CuO_4. (**b**) Possible primitive cell

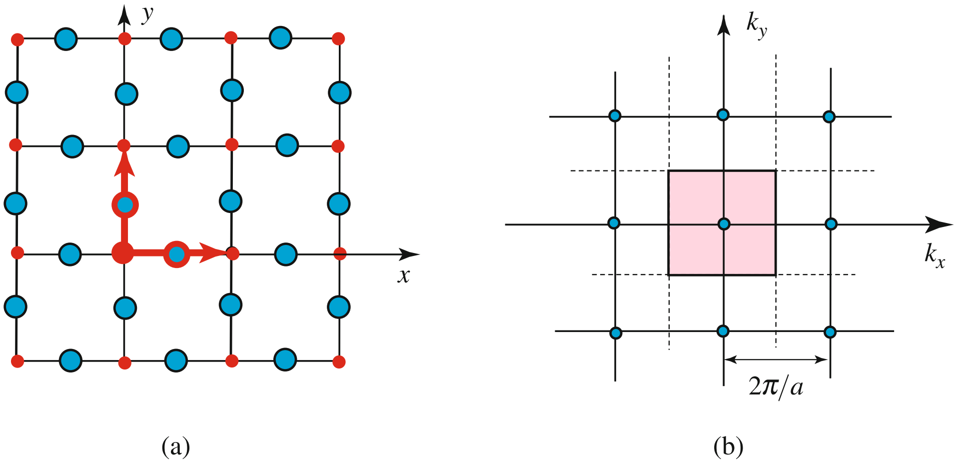
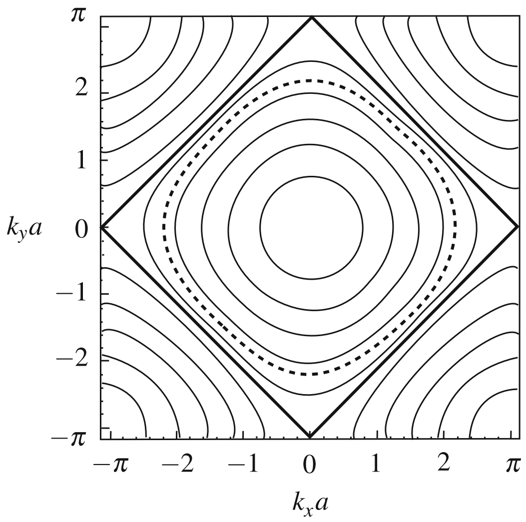


Fig. 2 (**a**) Square primitive cell of the CuO_2 plane. (**b**) Square reciprocal lattice and first Brillouin zone

Fig. 3 Constant energy curves and Fermi surface



which corresponds to

$$\cos k_x a = -\cos k_y a\,.$$

This is represented by the square in Fig. 3 which would be the Fermi surface of the corresponding metal.

5. Since neutrons and X rays do not give the same Bragg spots below 300 K, this suggests that *magnetic order* occurs at this temperature. The further spots obtained with neutron diffraction at the four points $(\pm\pi/a, \pm\pi/a)$ can be used to determine the reciprocal lattice of the magnetic order. It corresponds to a square lattice of side $\pi\sqrt{2}/a$, with area equal to half that of the reciprocal lattice of the crystal structure (see Fig. 4a). The real magnetic lattice thus has a unit cell of area $2a^2$, twice that of the crystal lattice. The ground state is therefore antiferromagnetic with two sublattices.

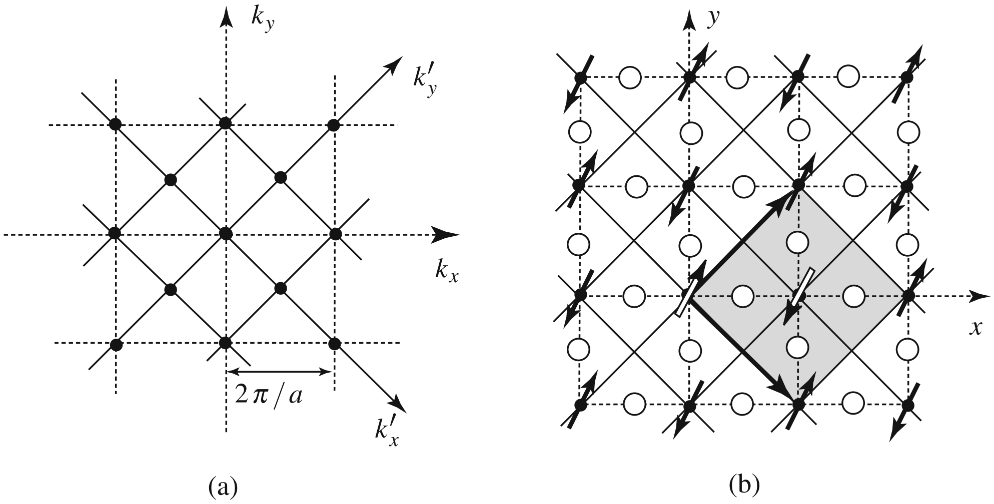


Fig. 4 (**a**) Reciprocal lattice of the magnetic structure. (**b**) Real space two-sublattice antiferromagnetic structure showing the primitive cell (*shaded*) and the two antiparallel Cu spin states of the magnetic basis

Since the La^{3+} and O^{2-} in the LaO planes donate one electron per primitive cell of the atomic structure to the CuO_2 plane, it seems likely that the electronegativity of the oxygen is satisfied and that the Cu is in a state Cu^{2+}, or $3d^9$. Therefore, the Cu^{2+} do carry the magnetic moment. The antiferromagnetic primitive cell is shown in Fig. 4b . This natural hypothesis regarding magnetism is borne out experimentally by measuring the intensities of the magnetic spots, which show that the corresponding structure factor is indeed that of Cu. The orientation of the moments in the unit cell cannot be obtained directly from this data, and are indeed more difficult to determine experimentally.

6. Replacing $x\mathrm{La}^{3+}$ by $x\mathrm{Sr}^{2+}$ amounts to transferring x fewer electrons per primitive cell to the CuO_2 planes. This seems to be enough to destroy the antiferromagnetic state and make the system metallic. Whereas one electron was lacking to saturate the $3d$ shell of Cu, $1+x$ are now lacking. Formally, there are therefore $1-x$ electrons or $1+x$ holes in the last occupied CuO_2 band. If we attempt to interpret this metallic state in a band model with $1-x$ electrons, this corresponds in the case $x = 0.15$ to a curve of constant E with area 0.85/2 times the area of the first Brillouin zone. This would be roughly the area enclosed by the dotted curve in Fig. 3 .

In reality, the compound La_2CuO_4 is a *Mott–Hubbard insulator*, and the holes created by substituting Sr are in fact holes on the oxygens in the planes. We are still a long way from understanding this type of metallic state, in which a magnetic moment associated with the hole on the Cu coexists with holes on the oxygen that play a dominant role in electron transport properties. The many conceptual difficulties sketched here explain in part the considerable effort required to understand the origins of high-T_c superconductivity.