Problem 1.

The compound with chemical formula La_2CuO_4 has the 3D structure with body-centered tetragonal conventional cell shown in Fig. 1. Note that it comprises a stack of LaO and CuO_2 planes.

1. *On Fig. 1, indicate the primitive vectors and basis of a primitive cell in the 3D crystal.*

The electronic configurations of the neutral atoms making up this structure are

$$\text{La}: \quad (\text{Xe})\ 5d^1\, 6s^2\,, \qquad \text{Cu}: \quad (\text{Ar})\ 3d^{10}\, 4s\,, \qquad \text{O}: \ 1s^2\, 2s^2\, 2p^4\,.$$

2. *According to an LCAO calculation, is this compound insulating or metallic?*

The LCAO calculation shows that the La and oxygen in the LaO planes are in the configurations La^{3+} and O^{2-} corresponding to fully occupied shells. Bands resulting from these orbitals are at energy levels well below those of the Cu($3d$) and O($2p$) bands of the oxygens in the CuO_2 planes. It is thus the latter that constitute the valence or conduction levels of the crystal. It therefore suffices to consider the electronic structure of the CuO_2 plane.

3. *Specify the primitive cell of the CuO_2 plane, along with its reciprocal lattice and first Brillouin zone.*

We shall assume that the last occupied band corresponds to one orbital per Cu site of atomic energy E_0. The band is calculated using the LCAO approximation, only taking into account nearest-neighbour hopping integrals t_0 and t_1.

4. *Find the eigenergies $E(k_x,k_y)$ and plot the constant energy curves in the first Brillouin zone. What is the curve corresponding to an occupancy of one electron per unit cell?*

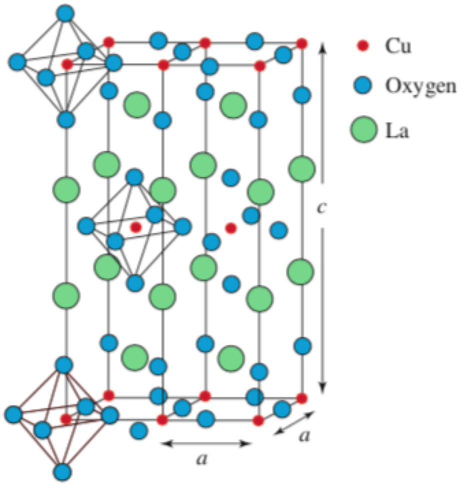


Fig. 1 Crystal structure of La_2CuO_4, showing body-centered tetragonal conventional cell

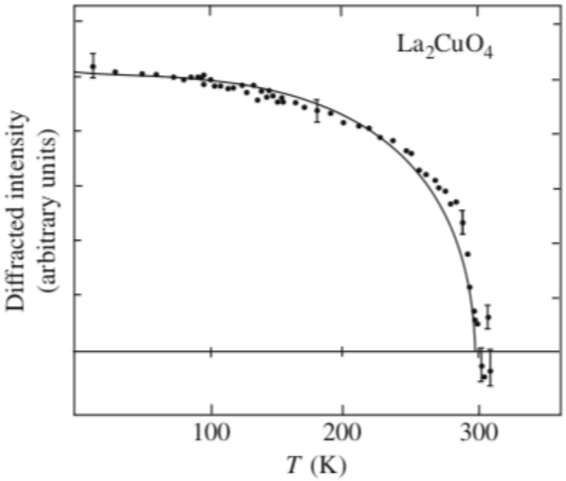


Fig. 2 Temperature dependence of the intensity of the neutron diffraction peak at $(\pi/a, \pi/a)$. Adapted from Yamada, K., Kudo, E., Endoh, Y., Hikada, Y., Oda, M., Suzuki, M., Murakami, T.: Solid State Commun. **64**, 753 (1987)

Conductivity measurements show that La_2CuO_4 is insulating. Moreover, neutron diffraction produces Bragg peaks at the four points $(\pm\pi/a, \pm\pi/a)$ of the plane below 300 K. The intensity of these peaks increases at low temperatures and saturates at $T = 0$ K, as shown in Fig. 2. X-ray diffraction only picks up the Bragg spots corresponding to the reciprocal lattice found in question 3.

5. *What can you deduce about the ground state of the electronic system of the CuO_2 plane? Specify the primitive cell of the real lattice of the CuO_2 plane for $T < 300\ K$.*

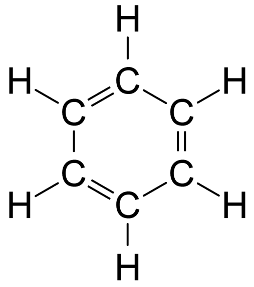
A fraction of the La^{3+} is replaced by Sr, which has the ionic form Sr^{2+} in the crystal. In the compound $La_{1.85}Sr_{0.15}CuO_4$ it is observed that the spots at the four points $(\pm\pi/a, \pm\pi/a)$ of the plane disappear in a neutron diffraction experiment. Moreover, this compound is superconducting with a critical temperature of 40 K.

6. *What conclusions can be drawn from these observations? According to the LCAO approximation, what should be the Fermi surface of this metal?*

LCAO = tight-binding

Problem 2. Huckel molecular orbital theory.

Apply the ideas of tight binding approximation and calculate the electronic structure of benzene.



1. Construct the ground state wave function out 6 p_z orbitals.

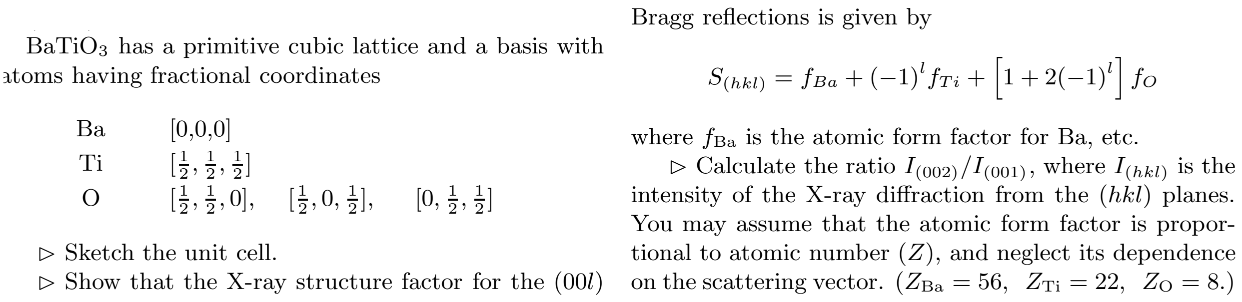
2. Including only nearest-neighbor approximation construct the Hamiltonian in the matrix form using a=<i|H|i> - the onsite energy and b=n-n overlap integral which is gamma in our lecture notes). Assume a=-11.2 eV and b= -0.7eV.

3. Calculate the energy levels and comment of the observed energy states.

4. Calculate *normalized* eigenvectors for those eigenstates. Comment on the meaning of “+” and “-“ of the individual components of the eigenvectors.

Problem 3.

One of the most important ferroelectrics is BaTiO3 which has perovskite structure.



$BaTiO_3$ has a primitive cubic lattice and a basis with atoms having fractional coordinates

Ba	[0,0,0]		
Ti	$[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$		
O	$[\frac{1}{2}, \frac{1}{2}, 0]$,	$[\frac{1}{2}, 0, \frac{1}{2}]$,	$[0, \frac{1}{2}, \frac{1}{2}]$

▷ Sketch the unit cell.

▷ Show that the X-ray structure factor for the $(00l)$ Bragg reflections is given by

$$S_{(hkl)} = f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O$$

where f_{Ba} is the atomic form factor for Ba, etc.

▷ Calculate the ratio $I_{(002)}/I_{(001)}$, where $I_{(hkl)}$ is the intensity of the X-ray diffraction from the (hkl) planes. You may assume that the atomic form factor is proportional to atomic number (Z), and neglect its dependence on the scattering vector. ($Z_{\mathrm{Ba}} = 56$, $Z_{\mathrm{Ti}} = 22$, $Z_{\mathrm{O}} = 8$.)

Problem 4.

Drude model.

Scattering Times

The following table gives electrical resistivities ρ, densities n, and atomic weights w for the metals silver and lithium:

	ρ (Ωm)	n (g/cm^3)	w
Ag	1.59×10^8	10.5	107.8
Li	9.28×10^8	0.53	6.94

▷ Given that both Ag and Li are monovalent (i.e., have one free electron per atom), calculate the Drude scattering times for electrons in these two metals.

In the kinetic theory of gas, one can estimate the scattering time using the equation

$$\tau = \frac{1}{n\langle v\rangle\sigma}$$

where n is the gas density, $\langle v\rangle$ is the average velocity (see Eq. 3.4 and σ is the cross-section of the gas molecule—which is roughly πd^2 with d the molecule diameter. For a nitrogen molecule at room temperature, we can use $d = .37$nm.

▷ Calculate the scattering time for nitrogen gas at room temperature and compare your result to the Drude scattering times for electrons in Ag and Li metals.

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} \quad (3.4)$$