CHAPTER 3

Density of states

In this chapter the density of states of the energy bands $E^{ap}_{\pm+}$ will be calculated from the definition. The definition of the density of states per unit area, not counting spin, is[13]

$$D(E) \qquad = \qquad (1/4\pi^2) \int d\vec{k}\, \delta(E-E_{\vec{k}}) \qquad\qquad (3.1)$$

The integration is over any primitive cell.

Instead of direct calculation on $E^{ap}_{\pm+}$, we calculate the reduced density of states, $g(\varepsilon)$, as a function of the reduced energy, ε. Using the relation between the density of states and the reduced density of states, we get the density of states, $\rho(E)$. The reduced energy, ε, is defined in the following way : we rewrite, from eq. (2.28) and eq. (2.29), the energy bands $E^{ap}_{\pm+}$ as

$$[\, E^{ap}_{\pm+} - (\frac{E_d + E_p}{2})\,]^2 - (\frac{E_d - E_p}{2})^2 = 4\gamma^2 \{\, \sin^2(\frac{k_x a}{2}) + \sin^2(\frac{k_y a}{2})\}$$

$$[\, E^{ap}_{\pm+} - (\frac{E_d + E_p}{2})\,]^2 - (\frac{E_d - E_p}{2})^2 = 2\gamma^2 \{\, 2\sin^2(\frac{k_x a}{2}) + 2\sin^2(\frac{k_y a}{2})\}$$

$$\frac{\left[E_{\pm+}^{ap} - \left(\frac{E_d + E_p}{2}\right)\right]^2 - \left(\frac{E_d - E_p}{2}\right)^2}{2\gamma^2} - 2 = -\cos(k_x a) - \cos(k_y a) \quad (3.2)$$

The reduced energy is defined by the equation

$$\mathcal{E}_{\vec{k}} = -\cos(k_x a) - \cos(k_y a) \quad (3.3)$$

According to eq. (3.2) , we also get

$$\mathcal{E}_{\vec{k}} = \frac{\left[E_{\pm+}^{ap} - \left(\frac{E_d + E_p}{2}\right)\right]^2 - \left(\frac{E_d - E_p}{2}\right)^2}{2\gamma^2} - 2 \quad (3.4)$$

The reduced density of states is now calculated. For a unit cell with area a^2, the reduced density of states, according to eq(3.1), is

$$g(\mathcal{E}) = \left(\frac{a}{2\pi}\right)^2 \iint_{B.Z.} \delta(\mathcal{E} - \mathcal{E}_{\vec{k}})\, dk_x dk_y \quad (3.5)$$

Substituting $\mathcal{E}_{\vec{k}}$, eq. (3.3), into eq. (3.5), we get

$$g(\mathcal{E}) = \left(\frac{a}{2\pi}\right)^2 \iint_{B.Z.} \delta(\mathcal{E} + \cos k_x a + \cos k_y a)\, dk_x dk_y \quad (3.6)$$

Let $X = \cos k_x a$ and $Y = \cos k_y a$ $\quad (3.7)$

We get

$$g(\mathcal{E}) = \left(\frac{a}{2\pi}\right)^2 \cdot \frac{1}{a^2} \iint dX dY [1 - X^2]^{-\frac{1}{2}} [1 - Y^2]^{-\frac{1}{2}} \delta(\mathcal{E} + X + Y)$$

$$g(\mathcal{E}) = \frac{1}{4\pi^2} \int dX [1 - X^2]^{-\frac{1}{2}} \int dY [1 - Y^2]^{-\frac{1}{2}} \delta(\mathcal{E} + X + Y)$$

$$g(\mathcal{E}) = \frac{1}{4\pi^2} \int dX [1 - X^2]^{-\frac{1}{2}} [1 - (\mathcal{E} + X)^2]^{-\frac{1}{2}} \quad (3.8)$$

We now consider the limits of integration of eq. (3.8).   To get the

limits of integration, we return to eq. (3.3). We have as the range of

ε : $-2 \leqslant \varepsilon \leqslant 2$. The reduced density of states is symmetric in ε

because of the cosine functions, therefore, we need consider only ε

in the range $0 < \varepsilon \leqslant 2$. For $0 < \varepsilon \leqslant 2$ we show in fig. 5 a curve

of constant ε in the (k_x, k_y) - plane
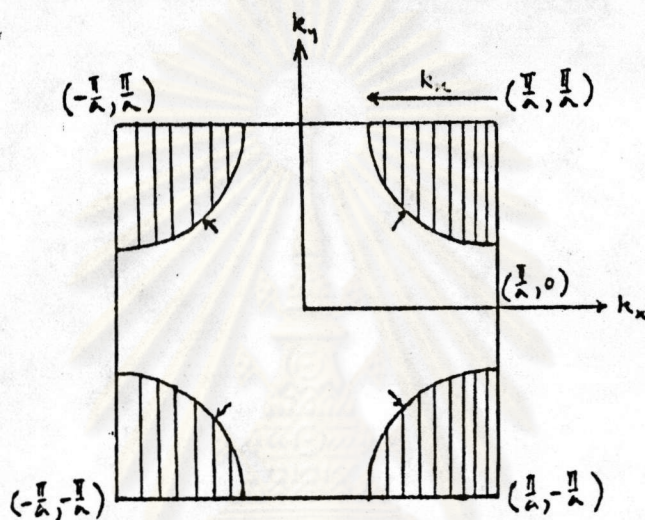

Fig. 5   a)   The square is a Brillouin zone

b)   The arrows indicate lines of constant ε in a

Brillouin zone

c)   The arrow with k_x above indicates limits of

integration with respect to k_x

The four parts of the curve of constant ε are symmetry, therefore,

we integrate along a part and multiply the integral by 4.   At the upper

right-hand side the limits of integration are $\frac{\pi}{a}$ and the point of

interception k_x.   Using eq. (3.7), we get the limits of integration

as $X = \cos(\frac{\pi}{a} \cdot a) = -1$ corresponding to the point $(\frac{\pi}{a}, \frac{\pi}{a})$ and

$X = \cos(k_x a) = -\cos(\frac{\pi}{a} \cdot a) - \varepsilon = 1 - \varepsilon$ corresponding to the point $(k_x, \frac{\pi}{a})$. Therefore eq. (3.8) becomes

$$g(\varepsilon) = \frac{4}{4\pi^2} \int_{-1}^{1-\varepsilon} dX [1 - X^2]^{-\frac{1}{2}} [1 - (\varepsilon + X)^2]^{-\frac{1}{2}} \tag{3.9}$$

Eq. (3.9) can be evaluated by using the transformation

$$X = \frac{2 - (1+\varepsilon)(2-\varepsilon) t^2}{(2-\varepsilon) t^2 - 2} \tag{3.10}$$

According to the transformation, we get

$$dX = dt \frac{4\varepsilon(2-\varepsilon) t}{[(2-\varepsilon) t^2 - 2]^2} \tag{3.11}$$

$$[1 - X^2]^{-\frac{1}{2}} = \frac{(2-\varepsilon) t^2 - 2}{[\varepsilon t^2 (2-\varepsilon)\{4 - (2+\varepsilon)(2-\varepsilon) t^2\}]^{\frac{1}{2}}} \tag{3.12}$$

$$[1 - (\varepsilon + X)^2]^{-\frac{1}{2}} = \frac{(2-\varepsilon) t^2 - 2}{[4\varepsilon(1-t^2)(2-\varepsilon)]^{\frac{1}{2}}} \tag{3.13}$$

With the limits of integration

$$X = -1 \qquad \text{for} \qquad t = 0$$
$$X = 1 - \varepsilon \qquad \text{for} \qquad t = 1$$

Substituting these results into eq. (3.9), we get

$$g(\varepsilon) = \frac{1}{\pi^2} \int_0^1 \frac{dt}{\sqrt{1-t^2}\sqrt{1-\{1-(\frac{\varepsilon}{2})^2\}t^2}}$$

or

$$g(\varepsilon) = \frac{1}{\pi^2} K\left(\sqrt{1-(\frac{\varepsilon}{2})^2}\right) \qquad (3.14)$$

where $K(k)$ is the complete elliptic integral of the 1st kind
with $k = \sqrt{1-(\frac{\varepsilon}{2})^2}$.

To get the density of states from the reduced density of
states, the relation between them must be known. This can be obtained
by using the properties of the δ - function. From eq. (3.4) we get

$$\delta(\varepsilon - \varepsilon_{\vec{k}}) = \delta\left(\frac{\left[E-(\frac{E_d+E_p}{2})\right]^2 - \left[E_{\vec{k}}^{ap}-(\frac{E_d+E_p}{2})\right]^2}{2\gamma^2}\right) \qquad (3.15)$$

The following identities are used:

1. $\delta(ax) = \frac{1}{|a|}\delta(x)$, $a \neq 0$

2. $\delta(x^2 - a^2) = \frac{1}{|2a|}(\delta(x-a) + \delta(x+a))$, $a \neq 0$

and eq. (3.15) becomes

$$\delta(\varepsilon - \varepsilon_{\vec{k}}) = 2\gamma^2 \delta\left([E-(\frac{E_d+E_p}{2})]^2 - [E_{\vec{k}}^{ap}-(\frac{E_d+E_p}{2})]^2\right)$$

$$\delta(\mathcal{E} - \mathcal{E}_{\vec{k}}) = \frac{\gamma^2}{\left| E_{\vec{k}}^{ap} - \left(\frac{E_d + E_p}{2}\right)\right|} \left[\delta(E - E_{\vec{k}}^{ap}) + \delta(E + E_{\vec{k}}^{ap} - 2 \cdot \frac{E_d + E_p}{2})\right]$$

$$\int_{\Omega} \delta(\mathcal{E} - \mathcal{E}_{\vec{k}})d\vec{k} = \int_{\Omega} d\vec{k} \frac{\gamma^2}{\left| E_{\vec{k}}^{ap} - \left(\frac{E_d + E_p}{2}\right)\right|} \left[\delta(E - E_{\vec{k}}^{ap}) + \delta(E + E_{\vec{k}}^{ap} - \frac{2(E_d + E_p)}{2})\right]$$

If $E = E_{\vec{k}}^{ap}$, then $\mathcal{E} = \mathcal{E}_{\vec{k}}$, and we get

$$\int_{\Omega} \delta(\mathcal{E} - \mathcal{E}_{\vec{k}})d\vec{k} = \frac{\gamma^2}{\left| E - \left(\frac{E_d + E_p}{2}\right)\right|} \int_{\Omega} \delta(E - E_{\vec{k}}^{ap})d\vec{k} \qquad (3.16)$$

Eq. (3.16) is the relation between the density of states and the reduced density of states. Since the density of states per unit cell is $(\frac{a}{2\pi})^2 \int_{B.Z.} \delta(E - E_{\vec{k}}^{ap})d\vec{k}$, we get from eq. (3.16),

$$\rho(E) = \frac{\left| E - \left(\frac{E_d + E_p}{2}\right)\right|}{\gamma^2} (\frac{a}{2\pi})^2 \int_{B.Z.} \delta(\mathcal{E} - \mathcal{E}_{\vec{k}})d\vec{k} \qquad (3.17)$$

where $\rho(E)$ is the density of states per unit cell and is equal to $(\frac{a}{2\pi})^2 \int_{B.Z.} \delta(E - E_{\vec{k}}^{ap})d\vec{k}$. Using eq. (3.5) and eq. (3.14), eq. (3.17) becomes

$$\rho(E) = \frac{\left| E - \left(\frac{E_d + E_p}{2}\right)\right|}{\gamma^2} \cdot \frac{1}{\pi^2} K(\sqrt{1 - (\frac{\mathcal{E}}{2})^2}) \qquad (3.18)$$

For the whole Cu-O plane with N unit cell, the density of states is, therefore,

$$N\rho(E) = \frac{N}{\pi^2} \cdot \frac{\left| E - \left(\frac{E_d + E_p}{2}\right)\right|}{\gamma^2} K(\sqrt{1 - (\frac{\mathcal{E}}{2})^2}) \qquad (3.19)$$

Further consideration can be made by replacing the complete elliptic integral with a series representation. The series representation to be used is

$$K(k) = \ln\frac{4}{k'} + (\frac{1}{2})^2(\ln\frac{4}{k'} - \frac{2}{1\cdot2})k'^2 + \ldots \qquad (3.20)$$

$$k' = \sqrt{1 - k^2} \qquad (3.21)$$

In this case $k^2 = 1 - (\frac{\varepsilon}{2})^2$ and, then, $k'^2 = (\frac{\varepsilon}{2})^2$. From eq. (3.20) we see that the density of states shows logarithmic singularity at $\varepsilon = 0$ (Fig.6). Eq. (3.4) gives us the energies corresponding to $\varepsilon = 0$,
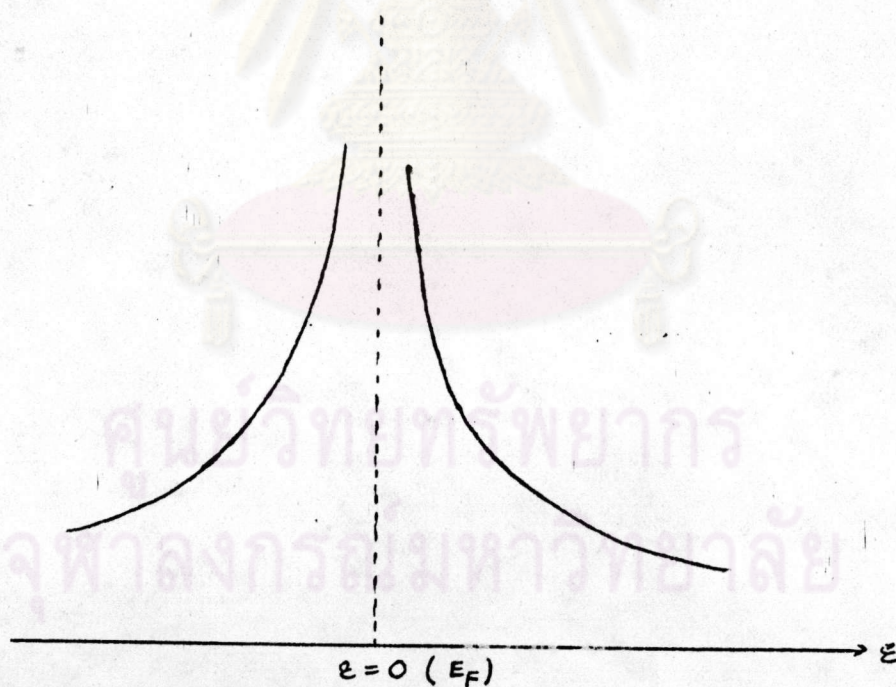
Fig.6   Density of states of the bands $E_{\pm}^{\varphi}$. The small asymmetry is due to the linear term of E.

they are

$$E_s^{\pm} = (\frac{E_d + E_p}{2}) \pm [(\frac{E_d - E_p}{2})^2 + 4\Upsilon^2]^{\frac{1}{2}} \qquad (3.22)$$

of the saddle points $|k_x| = \frac{\pi}{a}$ with $k_y = 0$, and $k_x = 0$ with $|k_y| = \frac{\pi}{a}$ in the reciprocal space. Actually, these singularities have their origins in the two-dimensional character of the model according to van Hove[14] , and they would remain even if the transfer integrals between the next neighbours in the plane are taken into account. In the pure La_2CuO_4, the copper ions are Cu^{2+} , the d-states should contain 9 electrons per copper atom in the ground state. The upper non-empty band is thus a half-filled band. We can easily see from eq. (2.28) and eq. (3.22) that the Fermi energy coincides with the logarithmic singularity at the energy E_s^+ of the band E_{++}^{ap} . This singularity exhibits a double degeneracy since it is associated to the two saddle points $(\frac{\pi}{a}, 0)$ and $(0, \frac{\pi}{a})$, in the tetragonal phase. We thus expect a band Jahn-Teller effect[15], which leads to a structural phase transition from the tetragonal phase to an orthorhombic one. In the orthorhombic phase, the energies of the two previous saddle points are different, and the logarithmic singularity is thus split into two distinct ones, with the Fermi energy lying between them, in a region where the density of states is low (Fig.7). Substitution in small amount of Ba to La i.e. $La_{2-x}Ba_xCuO_4$, or changing of density of oxygen vacancies i.e. La_2CuO_{4-y}, or both, is to increase the Cu^{3+}/Cu^{2+} ratio and thus shift the Fermi energy a little. Above some small critical ratio of Cu^{3+}/Cu^{2+}, the band Jahn - Teller effect disappears and makes the
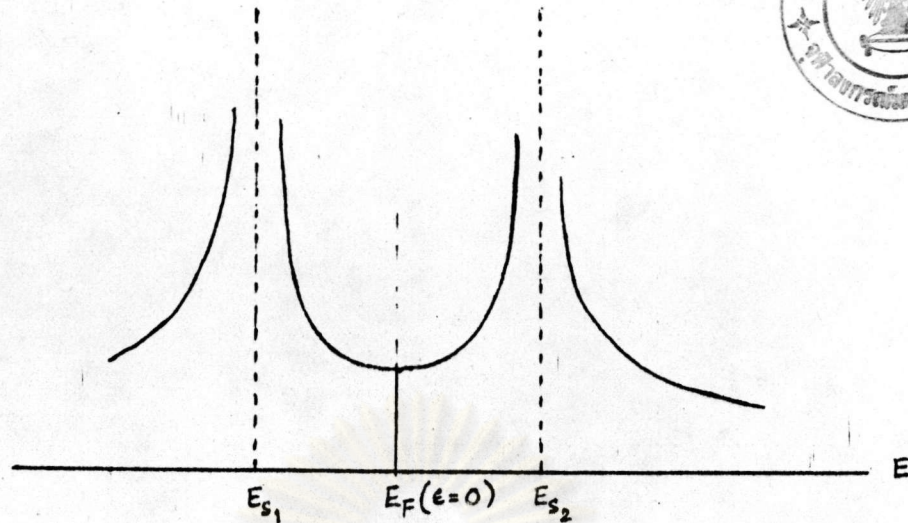
Fig.7 Density of states in the orthorhombic phase

orthorhombic phase unstable, the stable phase is them the tetragonal
one. As the Fermi energy E_F remains close to the singularity in this
phase, even though it does not exactly coincide with the singularity,
the density of states near E_F is much larger than in the orthorhombic
phase. The tetragonal phase is thus superconducting.

In the next chapter, the critical temperature, T_c, will be
computed by using the BCS theory. To compute the critical temperature,
we must know the density of states in the neighbourhood of the Fermi
level. Knowing that the pure La_2CuO_4, in the tetragonal phase, has the
Fermi energy coincides with the logarithmic singularity at the energy
E_s^+ , the density of states in the neighbourbood of the Fermi level is,
thus, the same as the density of states in the neighbourhood of E_s^+ .
To get the density of states in the neighbourhood of E_s^+ , we return to
eq. (3.4). The equation is rewritten as

$$\mathcal{E}_{\vec{k}} = \frac{\left[E_{\pm+}^{\alpha p}(\vec{k}) - \left(\frac{E_d + E_p}{2}\right) \right]^2 - \left[\left(\frac{E_d - E_p}{2}\right)^2 + 4\gamma^2 \right]}{2\gamma^2} \tag{3.23}$$

From eq. (3.22), we get

$$\left(\frac{E_d - E_p}{2}\right)^2 + 4\gamma^2 = \left[E_s^{\pm} - \left(\frac{E_d + E_p}{2}\right) \right]^2 \tag{3.24}$$

Substituting eq. (3.24) into eq. (3.23), for the band $E_{++}^{\alpha p}(\vec{k})$, we get

$$\mathcal{E}_{\vec{k}} = \frac{\left[E_{++}^{\alpha p}(\vec{k}) - \left(\frac{E_d + E_p}{2}\right) \right]^2 - \left[E_s^{+} - \left(\frac{E_d + E_p}{2}\right) \right]^2}{2\gamma^2}$$

$$\mathcal{E}_{\vec{k}} = \frac{\left[E_{++}^{\alpha p}(\vec{k}) - E_s^{+} \right]\left[E_{++}^{\alpha p}(\vec{k}) + E_s^{+} - \frac{2(E_d + E_p)}{2} \right]}{2\gamma^2} \tag{3.25}$$

From eq. (3.19) and eq. (3.20), we see that the density of states, in terms of $\mathcal{E}_{\vec{k}}$, can be written as

$$N\rho(E) = \frac{N}{\pi^2} \cdot \frac{\left| E - \left(\frac{E_d + E_p}{2}\right) \right|}{\gamma^2} \left[\ln\frac{8}{\mathcal{E}_{\vec{k}}} + \left(\frac{1}{2}\right)^2 \left(\ln\frac{8}{\mathcal{E}_{\vec{k}}} - \frac{2}{1\cdot 2} \right)\left(\frac{\mathcal{E}_{\vec{k}}}{2}\right)^2 + \cdots \right] \tag{3.26}$$

In the neighbourhood of E_s^{+}, $\mathcal{E}_{\vec{k}} \rightarrow 0$, and we get, approximately,

$$N^{\cdot}(E) \cong \frac{N}{\pi^2} \frac{\left| E_s^{+} - \left(\frac{E_d + E_p}{2}\right) \right|}{\gamma^2} \ln\frac{8}{\mathcal{E}_{\vec{k}}} \tag{3.27}$$

We also get, from eq (3.25),

$$\lim_{E_{++}^{\alpha p} \rightarrow E_s^{+}} \mathcal{E}_{\vec{k}} = \frac{\left[E_{++}^{\alpha p}(\vec{k}) - E_s^{+} \right]\left[2E_s^{+} - \frac{2(E_d + E_p)}{2} \right]}{2\gamma^2} \tag{3.28}$$

Substituting eq. (3.28) into eq (3.27), we get

$$N\rho(E) \simeq \frac{N}{\pi^2} \cdot \frac{\left| E_s^+ - \left(\frac{E_d + E_p}{2}\right) \right|}{\gamma^2} \ln\left(\frac{16\gamma^2}{\left| E_{++}^{ap}(\vec{R}) - E_s^+ \right| \left| 2E_s^+ - 2\left(\frac{E_d + E_p}{2}\right) \right|} \right) \qquad (3.29)$$

Define
$$D = \frac{\gamma^2}{2\left| E_s^+ - \left(\frac{E_d + E_p}{2}\right) \right|} \qquad (3.30)$$

In form of D , eq. (3.29) becomes

$$N\rho(E) \simeq \frac{N}{2\pi^2 D} \ln\left(\frac{16\,D}{\left| E_{++}^{ap}(\vec{R}) - E_s^+ \right|} \right)$$

or
$$N\rho(E) \simeq \frac{N}{2\pi^2 D} \ln\left(D \left| E_{++}^{ap}(\vec{R}) - E_s^+ \right|^{-1} \right) \qquad (3.31)$$

Eq. (3.31) shows the density of states in the neighbourhood of E_s^+ and it will be used, in the next chapter, to calculate the critical temperature.