## The band theory of Solids



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alternative-approach-to-the-problem-of-cnt-electron-energy-band-structure



Figure 4.1: Atomic chain

Let's consider a chain of  $N \gg 1$  identical atoms separated by a distance *a*. Let's assume that each atom *n* has only one electronic orbital  $\phi_n(r)$  (labeled by its ket  $|\phi_n\rangle$ ) which form a complete orthonormal basis. On this basis set the only matrix elements of the Hamiltonian are:

$$
\begin{cases}\n\langle \phi_m | H | \phi_{m+1} \rangle = \langle \phi_{m+1} | H | \phi_m \rangle = -t \\
\langle \phi_m | H | \phi_m \rangle = \varepsilon_0\n\end{cases}
$$

where  $t > 0$  denotes the amplitude of an electron hopping between adjacent orbitals. The electron wavefunction can be then decomposed on the atomic orbital basis:

$$
\left|\Psi\right\rangle =\sum_{m}c_{m}\left|\phi_{m}\right\rangle
$$

- 1. Find the relation between the coefficients  $c_m$  for a given Bloch wavevector  $k$ . (Hint: use the translational invariance of the atomic orbitals and the Bloch theorem).
- 2. Write down the eigenvalue equation and determine the "electronic dispersion"  $\varepsilon_k$ . Sketch  $\varepsilon_k$  in the first Brillouin zone. What's the bandwidth? Mark it on the drawing.
- 3. Find the effective mass of the electrons at the band bottom, close to  $k = 0$ .
- 4. Let's assume that the atoms are monovalent (i.e. there is only one electron on average for each  $|\phi_n\rangle$ ). Where is the Fermi level  $\varepsilon_F$ ? Say if the system is a metal or an insulator and explain your arguments.
- 5. Determine the total  $T = 0$  groundstate energy  $E_0$  of the monovalent atomic chain. Compare the average energy per atom with the bandwidth.

### 4.2 Peierls Instability

Let's consider a chain of *N >>* 1 identical atoms and assume that each atom *n* has only one electronic orbital  $\phi_n(r)$ , which is labeled by its ket  $|\phi_n\rangle$ . The chain is distorted, with the atomic distances alternating between  $a_1$  and  $a_2$  ( $a_1 + a_2 = 2a$ ,  $a_1 > a_2$ ).



Figure 4.2: Distorted atomic chain

 $|\phi_n\rangle$  form an orthonormal basis set and the only non-zero matrix elements are:

$$
\begin{cases}\n\langle \phi_{2m} | H | \phi_{2m+1} \rangle = \langle \phi_{2m+1} | H | \phi_{2m} \rangle = -t(1-\eta), \\
\langle \phi_{2m} | H | \phi_{2m-1} \rangle = \langle \phi_{2m-1} | H | \phi_{2m} \rangle = -t(1+\eta), \\
\langle \phi_{2m} | H | \phi_{2m} \rangle = \langle \phi_{2m+1} | H | \phi_{2m+1} \rangle = \langle \phi_{2m-1} | H | \phi_{2m-1} \rangle = \varepsilon_0 = 0\n\end{cases}
$$

To the first order, the distortion parameter  $\eta > 0$  is proportional to  $a_1 - a_2$ . For sake of simplicity we choose the orbital energies  $\varepsilon_0 = 0$ .

- 1. Explain succinctly why the matrix elements above can be written in this form. Determine the first Brillouin zone.
- 2. The electronic wavefunction can be decomposed on the atomic orbital basis

$$
|\Psi\rangle = \sum_{m} \alpha_{m} | \phi_{2m} \rangle + \beta_{m} | \phi_{2m+1} \rangle.
$$

By using the Bloch theorem and the translational invariance of the orbital wavefunctions  $|\phi_{2m}\rangle$  and  $|\phi_{2m+1}\rangle$ , find the ratios between the coefficients  $\alpha_m/\alpha_0$  and  $\beta_m/\beta_0$  for a given Bloch wavevector *k*.

- 3. Write down the eigenvalue equation. By projecting separately on  $\langle \phi_0 |$  and  $\langle \phi_1 |$  determine the energy spectrum  $\varepsilon(k)$  and draw it in the first Brillouin zone. Remember that in general a square root has two real solutions.
- 4. Let's suppose that there is only one electron in each atomic orbital  $\phi_n(r)$  (atoms are monovalent). Where is the last occupied level of  $\varepsilon(k)$ ? Mark the Fermi level. Is it the system in a metallic or insulating state?
- 5. Write down an integral expression of the total ground-state energy *E*1. Evaluate it in the small  $\eta$  limit by using the expression  $\int_0^{\frac{\pi}{2}} dx \sqrt{1-(1-\alpha^2)\sin^2 x} \approx 1+\frac{\alpha^2}{2} \left[ln\left(\frac{4}{\alpha}\right)-\frac{1}{2}\right],$ valid for  $\alpha \ll 1$ .
- 6. Let's consider the total energy  $E_0$  of the undistorted chain  $(a_1 = a_2 = a)$ . Evaluate the sign of  $E_1 - E_0$  and draw a conclusion about what is the most energetically favorable state of the chain from the electronic viewpoint.

7. The structure and the conductivity of KCP  $(K_2[Pt(CN)_4]Br_{0.3} 3H_2O)$  are displayed in Fig. 4.2. Explain why KCP can be well described by a one-dimensional tight-binding model. What's the orbital represented by  $|\phi_n\rangle$ ? Give an interpretation of the behavior of the conductivity (here we show the log of conductivity as a function of 1*/T*). Is KCP insulating or conducting under 150K? Say what happens at 150K.



Figure 4.3:  $K_2[Pt(CN)_4]Br_{0.3} 3H_2O$ 

### 4.3 Square lattice in 2D

Let's consider a square lattice of atoms in two dimensions (2D). Each atom position can be labeled by  $\vec{R} = m \vec{a}_x + n \vec{a}_y$ , being  $\vec{a}_x, \vec{a}_y$  ( $|\vec{a}_x| = |\vec{a}_y| = a$ ) the lattice generating vectors and  $m, n \in \mathbb{N}$ . Let's assume that each atom  $(m, n)$  has only one electronic orbital  $\phi_{m,n}(r)$  (its ket being  $|\phi_{m,n}\rangle$  forming a complete orthonormal basis. On this basis set the only matrix elements of the (hermitian) Hamiltonian are:

$$
\begin{cases}\n\langle \phi_{m,n} | H | \phi_{m\pm 1,n} \rangle = \langle \phi_{m,n} | H | \phi_{m,n\pm 1} \rangle = -t \\
\langle \phi_{m,n} | H | \phi_{m,n} \rangle = \varepsilon_0 = 0\n\end{cases}
$$

where  $t > 0$  denotes the amplitude of an electron hopping between adjacent orbitals. The electron wavefunction can be then decomposed on the atomic orbital basis:

$$
|\Psi\rangle = \sum_{m,n} c_{m,n} | \phi_{m,n} \rangle
$$

- 1. Find the relation between the coefficients  $c_{m,n}$  for a given Bloch wavevector  $\vec{k} = (k_x, k_y)$ . (Hint: use the translational invariance of the atomic orbitals and the Bloch theorem).
- 2. Determine and draw the first Brillouin zone.
- 3. Write down the eigenvalue equation and determine the electronic dispersion  $\varepsilon_{\vec{k}}$ . Sketch  $\varepsilon_{\vec{k}}$  along the direction  $(0,0) \to (\frac{\pi}{a}, \frac{\pi}{a}) \to (\frac{\pi}{a}, 0) \to (0,0)$  (the symmetry axis and the zone boundary) in the first Brillouin zone. What's the bandwidth? Mark it on the drawing.
- 4. Sketch in the  $(k_x, k_y)$  plane the lines of constant energy  $\varepsilon_{\vec{k}}$ , first close to the band minimum, then close to the band maximum, finally for  $\varepsilon_{\vec{k}} = 0$ .
- 5. Determine the effective mass close to the band minimum and maximum. Give also the density of states in these regions.
- 6. The density of states close  $\varepsilon_{\vec{k}} = 0$  is given by  $g(\varepsilon) = \frac{2}{\pi} g_0 \ln(\frac{16t}{|\varepsilon|})$  where  $g_0$  is the density of states close to the band maximum and minimum which was calculated above. Sketch the qualitative behavior of  $g(\varepsilon)$ .



Figure 4.4:  $CuO<sub>2</sub>$  plane in a cuprate superconductor

- 7. Let's suppose that the atoms are monovalent. Mark the Fermi level on the drawing of  $g(\varepsilon)$ . How many electrons per atom do we need in order to completely fill up the band?
- 8. As example of such square lattice system we consider the high-temperature cuprate superconductors (Fig. 4.4). These materials have a layered structure formed by  $CuO<sub>2</sub>$ planes which are only weakly coupled. The conduction takes mainly place within these planes, hence, under the electronic point of view, the cuprates can in first approximation be considered as 2D systems. The Cu valence electron is located in a  $d_{x^2-y^2}$  orbital, while the one of the oxygen is in a 2p orbital. It has been shown <sup>1</sup> that the  $p - d$ hybridization may reduce this  $CuO<sub>2</sub>$  system to an effective model with just one effective orbital (resulting from the  $p - d$  hybridization) at each site of a square lattice. This orbital is on average occupied by only one electron. According to Bloch band theory, should the system be in a metallic or an insulating state?

<sup>1</sup>F.C. Zhang, T.M. Rice, *E*ff*ective Hamiltonian for the superconducting Cu oxides*, Phys. Rev., B 37, 3759 (1988).

# Semiconductors





The first junction Years  $90s : 10^{11}$  transistors From the periodic transistor (Bell Labs, 1950) on a disk of diameter 20 cm table of elements on a disk of diameter 20 cm

aluminius	silicium	hese
13	14	15
Al	Si	o
26.98153	28,0855	30.973762
allium	14199	形成的
31	32	33
Ga	Ge	As
69.723	72.61	74,92160
indium 114,818	étain 50 Sn 118,710	intimaini 51 Sb 121,760

In this chapter we are going to study the behavior of the resistivity in semiconductors as a function of temperature *T*. We shall focus in particular on the role played by impurities, which is fundamental for technological applications.

We will use the following **notation**:

- $\varepsilon_c$ : electron energy at the bottom of the conduction band (BC)
- $\varepsilon_v$ : electron energy at the top of the valence band (BV)
- $\varepsilon_g = \varepsilon_c \varepsilon_v$ : gap energy
- *m* : electron mass
- $e$ : electron charge  $(e > 0)$
- *m<sup>c</sup>* : effective mass at the bottom of the conduction band
- *m<sup>h</sup>* : hole effective mass in the valence band

• 
$$
N_0 = \frac{1}{\sqrt{2}} \left(\frac{m}{\pi \beta \hbar^2}\right)^{3/2} = 2.42182 \times 10^{25}; N_c = N_0 \left(\frac{m_c}{m}\right)^{3/2}; N_h = N_0 \left(\frac{m_h}{m}\right)^{3/2}
$$

•  $\mu_e$  and  $\mu_h$ : electron and hole mobility respectively

In general for an intrinsic or extrinsic semiconductor, the electron  $(n_c)$  and hole  $(n_h)$  densities are given by:

$$
n_c(T) = N_c \exp\left[-\beta(\varepsilon_c - \mu)\right] \qquad n_h(T) = N_h \exp\left[-\beta(\mu - \varepsilon_v)\right] \tag{5.1}
$$

where  $\mu(T)$  is the electron chemical potential.

### 5.1 Resistivity of Intrinsic Semiconductors

The first 2 questions (not numbered) have been already treated during the course. You can skip them if you already know the answers.

The free carriers in an intrinsic (pure) semiconductors are given on one side by the electrons, which are thermally excited from the valence to the conduction band, and on the other side by the holes left in the in the valence band by excited electrons. In this case we have then  $n_c(T) = n_h(T) \equiv n_i(T)$ .

- Show that  $n_i(T)$  only depends on the gap-energy  $\varepsilon_q$ , the temperature *T*, and  $N_c$ ,  $N_h$ . In particular, it does not depend on the chemical potential  $\mu$ .
- By using the relation above between  $n_c(T)$  and  $n_i(T)$  show that the chemical potential in a intrinsic semiconductor is (within a good approximation) in the middle of the gap.
- 1. Compare the number of charge carriers  $n_i(T)$  of Ge at room temperature ( $\varepsilon_q = 0.67$  eV,  $m_c/m = 0.55$ ,  $m_h/m = 0.29$ ) with the one of Cu (imagine one electron per unit cell, the order of magnitude is enough).
- 2. The mobility of Ge at room temperature is  $\mu_e = 3600 \text{ cm}^2/\text{Vs}$  for the electrons and  $\mu_h = 1800 \text{ cm}^2/\text{Vs}$  for the holes. Give an order of magnitude of the conductivity of Ge at room temperature. Compare it with the conductivity of Cu, whose electron mobility  $\mu_e = 44, 5 \text{ cm}^2/\text{Vs}$  is much smaller than the one of Ge. Are then intrinsic semiconductors good conductors at room temperature ?
- 3. Carrier mobility depends in general on temperature. We shall assume that at room temperature the phonons dominate the carrier scattering. We have then  $\mu_{e,h}(T) \propto T^{-3/2}$ . Give an expression of the conductivity and of the resistivity as a function of *T*. Compare with figure 5.1, which displays the temperature-dependence of the resistivity of Ge. Can you explain the behavior of the curve labeled "1", which is the most pure sample? From this curve we can also extract the value of the gap  $\varepsilon_q$ . Explain how.

### 5.2 Resistivity of Extrinsic Semiconductors

Semiconductors in applications are generally doped. A  $n$ -type semiconductor is doped with atoms (donors) releasing electrons. In this case we shall call the donor concentration  $N_d$ , the donor energy level  $\varepsilon_d$  and the number of ionized donors (which have actually released electrons into the conduction band)  $n_d(T)$ . Conversely, a *p*-type semiconductor is doped with atoms which absorb electrons (acceptors). In this case we shall call the acceptor concentration  $N_a$ , the acceptor energy level  $\varepsilon_a$  and the number of ionized acceptors (which have actually left holes into the valence band)  $n_a(T)$ .

- 1. We have typically  $\varepsilon_c \varepsilon_d = 12.7$  meV for a *n*-type and  $\varepsilon_a \varepsilon_v = 10.8$  meV for *p*-type Ge semiconductor. Draw a schema representing, for both  $n$ -type and  $p$ -type cases, the energy levels  $\varepsilon_c$ ,  $\varepsilon_v$ , and  $\varepsilon_a$  or  $\varepsilon_d$ . Say if at room temperature doped Ge is a conductor or an insulator.
- 2. Which dopant should we use in order to have  $n$ -type Ge, As or Ga (look at the periodic table)?
- 3. Write the generic relation between  $n_c$ ,  $n_h$  and  $n_d$  ( $n_c$ ,  $n_h$  and  $n_a$ ) for a  $n$ -type ( $p$ -type) semiconductor. The number of free carriers  $n_c$  and  $n_h$  are in general *T*-dependent. How do the above relations simplify for a  $n$ -type ( $p$ -type) semiconductor in the limit  $N_d >> n_h$  ( $N_a >> n_c$ ) and  $k_B T >> \varepsilon_c - \varepsilon_d$  ( $k_B T >> \varepsilon_a - \varepsilon_v$ )?
- 4. We consider now a  $n$ -type semiconductor (the  $p$ -type is treated in a similar way) in the so called *extrinsic regime*, for which  $\varepsilon_c - \varepsilon_v \gg k_B T \gg \varepsilon_c - \varepsilon_d$ . In this case we can also assume that  $n_d \gg n_h$ . Find the *T*-dependence of the resistivity considering that in this temperature range the electron scattering is dominated by impurities and the mobility  $\mu_e \sim T^{\frac{3}{2}}$ .
- 5. What happens to the *T*-dependence of the resistivity at high temperature  $k_B T$  >>  $\varepsilon_c - \varepsilon_v$ ?



Figure 5.1: Resistivity of Ge as a function of  $1/T$ , for different concentrations of antimony: for the curves labeled 1-29, the density of the donor atoms varies from  $5.3 \times 10^{20}$  m<sup>-3</sup> to  $9.5 \times 10^{23}$  m<sup>-3</sup> (figure extracted from Solid State Physics, Ashcroft and Mermin, originally from H. J. Fritzsche, J. Phys. Chem. Solids 6, 69, 1958).

6. By analogy with the intrinsic case, guess the  $T$ -dependence of the resistivity at low temperatures, when  $k_B T \leq \varepsilon_c - \varepsilon_d$ . Can you finally explain the qualitative behavior of the resistivity as a function of temperature for the doped Ge, displayed in Fig. 5.1?

### 5.3  $p - n$  junction: the diode



Figure 5.2: Schema of a  $p - n$  junction

Nowadays half on industrial research in materials is focused on microelectronics, whose building block is the transistor. Here we present a simple basic example of the transistor, the  $p - n$ junction, which has uncountable applications: diodes, used to stabilize tensions or to create continuous tensions, LEDs (light emitting diodes), solar cells, bipolar transistors which are used for example to amplify electric signals (as in your hi-fi),...

Let's consider then a semiconductor (like Si or Ge) in the extrinsic regime (all impurities are ionized). The semiconductor is  $p$ -doped on one side (the P side) and  $n$ -doped on the other (the N side), as displayed on Fig. 5.2. At the interface between the two regions a  $p-n$  junction forms. At the equilibrium the electrons gas must have the same chemical potential, i.e. the same Fermi energy, on both side of the junction. Therefore there should be a region around the junction where  $\varepsilon_c$  and  $\varepsilon_v$  change continuously from the P to the N side, as displayed in Fig. 5.2. We shall focus on the conduction band electrons (similar considerations hold for the holes in the valence band).

1. The intermediate region between the P and N side has no free carrier (we call it the depletion region). It is literally emptied of electrons/holes (the minus and plus signs that remain sketched in the green P and red N regions are the remaining static charges, once hole/electrons have escaped from the region). Explain why.

- 2. Such a situation can be described imagining that a difference of potential  $V_d \sim 1$  V sets up between the P and N sides. In which direction is the corresponding electric field *E*? (remember that  $\vec{E} = -\nabla V$ ). You may then describe in first approximation the junction as a capacitor having charged plates, with the free carriers (electrons and holes) accumulating as depicted in the bottom of Fig. 5.2.
- 3. With the effect of temperature there are thermal fluctuations. So it may happen that some (few) electrons (we are always focusing on the conduction band) gain enough thermal energy to win the potential energy gap and jump from the N side (the positive plate of the capacitor) to the P side (the negative plate of the capacitor). Such a process induces a current (remember that the convention is that the sense of the current is the one of positive charges) which has form typical of through-a-gap probability  $I_{P\rightarrow N}^{0} = I_0 \exp(-eV_d/k_B T)$ . On the other hand, it happens that some few electrons on the P side can enter by random processes into the depletion region, and at this point the are attracted to the N side. There is then another current  $I_{N\to P}^0$ . Find the relation between  $I_{P\to N}^0$  and  $I_{N\to P}^0$  at the equilibrium at temperature *T*.
- 4. We now apply a tension *U* to the junction (lets insert the junction into a circuit with a battery), such that the total tension is now  $V_d - U$ . Find the new expression of the current  $I_{P\to N}(U)$  as a function of  $I_{P\to N}^0$ . We assume that the (local) random processes which determine the  $I_{N\to P}^0$  are not much affected by *U*, hence  $I_{N\to P}(U) \simeq I_{N\to P}^0$ . Find an expression of the total neat current  $I_{tot}(U)$  through the junction and sketch it as a function of of the applied voltage *U*. You should discover the basic property of a diode.

# Superconductivity



Magnet levitating above a superconductor. From http://www.wou.edu/ rmiller09/superconductivity/

### 6.1 Thermodynamics

Experimentally we observe that if the magnetic field applied to a type-I superconductor is higher than a critical value  $H_c(T)$  the Meissner effect disappears. The temperature-behavior of  $H_c(T)$  (if T is not too low) is well described by the phenomenological formula:

$$
H_c(T) \simeq H_c(T=0) \left[ 1 - \left(\frac{T}{T_c}\right)^2 \right]
$$
\n(6.1)

#### 6.1.1 Magnetic-field-driven transition at  $T=0$

The Gibbs free energy variation per unit volume is given by  $dG = -SdT - \mu_0 MdH$ , for small temperature and magnetic-field variations.

1. Let's consider a isotherm transformation. Show that the Gibbs free energy of the superconductor under the application of the field  $H_a$  is given by: :

$$
G(H_a) = G(0) - \mu_0 \int_0^{H_a} M dH \qquad (6.2)
$$

- 2. What's the value of the magnetization of a superconductor at  $T = 0$  for  $H_a \lt H_c$ ? Infer the Gibbs free  $G_s(H_a)$  of the superconducting phase under the application of the field *Ha*.
- 3. Give the expression of the Gibbs free energy in a normal phase *G<sup>n</sup>* under the application of the field *Ha*, by introducing Pauli susceptibility. Compare the order of magnitude of this latter with the typical value of the susceptibility in the superconducting phase.
- 4. We know that for  $H_a = 0$  the ground-state is the superconducting state. Therefore  $\Delta G = G_n(H_a = 0) - G_s(H_a = 0) > 0$ . Can you give a physical meaning to this quantity? Remember the comparison above on the Pauli susceptibility in the normal and superconducting phases. Sketch the behavior of  $G_s$  and  $G_n$  en function of  $H_a$ . At which value  $H_c$  do these curves cross? What's the groundstate for  $H > H_c$ ? Give an expression of  $H_c$  as a function of  $\Delta G$  for  $T=0$ .

### 6.1.2 *H*-*T* phase diagram

Sketch in the  $H - T$  plane the line of coexistence between the superconducting and normal phases. The thermodynamic equilibrium between these two phase requires that  $G_s(T, H_c)$  $G_n(T, H_c)$ . By considering a small variation along the coexistence line (in this case the variation in temperature  $dT$  and in magnetic field  $dH = dH_c$  are constrained) find the transition latent heat  $L = T(S_n - S_s)$ . Consider in particular the cases  $T = 0$  and  $0 < T < T_c$ , what happens to the latent heat in this case? Can you say what is "the order of the transition" ?

#### 6.1.3 Specific Heat

Figure 6.1 displays the specific heat of aluminum in the superconducting and normal phases. Normal phase has been induced under *T<sup>c</sup>* by applying a weak magnetic field which destroys superconductivity.



Figure 6.1: From *Solid State Physics*, Ashcroft and Mermin, Harcourt, 1976.

- 1. What relevant physical quantity can we extract from the measure of the specific heat as a function of temperature in the superconducting phase (the applied magnetic field is in this case zero)?
- 2. The specific heat s given by  $C = T \frac{\partial S}{\partial T}$ . Write down  $C_s C_n$  as a function of the temperature  $T$  and of  $T$ -derivatives of  $S<sub>s</sub>$  and  $S<sub>n</sub>$ .
- 3. By using the result of the previous section on the latent heat *L*, show that:

$$
C_s - C_n = -2T\mu_0 \left(\frac{H_c(0)}{T_c}\right)^2 \left[1 - 3\left(\frac{T}{T_c}\right)^2\right]
$$
 (6.3)

4. Apply the formula 6.3 above at  $T = T_c$ , find the value of the specific heat jump. What relevant physical quantity related to the response of the superconductor to an applied magnetic field can you derive from this expression (without applying a priori any magnetic field!)?

### 6.2 Magnetic-field penetration into a type-I superconducting plate

A superconductor repels an external magnetic field (Meissner effect). By using London equations, show that the penetration of the magnetic induction vector  $\vec{B}$  into a superconductor is given by:

$$
\Delta \vec{B} = (1/\lambda_L^2) \vec{B} \tag{6.4}
$$

where  $\lambda_L = \sqrt{m/(\mu_0 n e^2)}$  is the London penetration depth (*m* and *e* are the electron mass and charge respectively, *n* the electron density) which is typically of the order of 100 nm.



Figure 6.2: "Thin" type-I superconducting plate

Let's consider now the case of a thin infinite  $(L \to \infty)$  plate of thickness 2*a*, as shown in Fig. 6.2, and let's apply an external constant magnetic field whose induction is  $\vec{B}$ .

- 1. Then inside the superconducting plate  $\vec{B}$  is modified. However  $\vec{B}$  can only depend on *x*. Explain why.
- 2. Show that only the components *y* and *z* can penetrate within the superconductor. We shall call  $\vec{B}_a$  the projection of *B* on the  $y - z$  plane.
- 3. Prove that

$$
\vec{B}(x) = \vec{B}_a \frac{\cosh(x/\lambda_L)}{\cosh(a/\lambda_L)}\tag{6.5}
$$

and sketch it as a function of *x*.

4. Derive the supercurrent  $\vec{j}_s$ . We consider that  $j_s = 0$  if  $B_a = 0$ . Where are the currents located? Sketch them on the drawing.