

The cuprate superconductors: generalities (composition, structure, phase diagram ...)

*Cuprates**: only materials currently known to be SC above boiling point (77K) of liquid nitrogen \Rightarrow enormous practical as well as theoretical interest (Ex: SQUIDS for geophysical properties). Not all cuprates are superconductors, but ~ 300 different materials so far known, with T_c ranging from a few K (original Bi-2201 samples) to ~ 160 K (Hg-1223 under 20 GPa). T_c of 110 – 120K in dozens of different materials.

Books etc.: Shaked et al., ANL ‘pocket-book’. Ginsberg, D.M., ed., Physical Properties of High Temperature Superconductors, volumes I-V, WS, Singapore, 1989-96; various conference proceedings etc.; Tinkham Ch. 9 for macroscopic EM properties.

General caution: beware of texts written by theoreticians! Almost any theory can be defended by concentrating on sufficiently limited set of experimental data + dismissing rest as result of bad samples etc.

Experimental pitfalls: multiphase samples, surface effects, extreme doping dependence ...

Composition: The traditional chemical notation, in which one simply specifies the composition in terms of the relative concentration of different elements (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$) is not really the most appropriate for the cuprates, as it doesn’t bring out their special structures. More appropriate is a formula of the type $(\text{CuO}_2)_n\text{A}_{n-1}\text{X}$.

Here A is an alkaline earth, a rare earth, Y or (occasionally) La, or a mixture of these elements. X is some other combination of elements, often not in stoichiometric proportions, it always[†] contains O and may also contain Cu and/or AE/RE elements. Thus, for example, in this notation $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ would have $n=2$, $\text{A}=\text{Y}$, $\text{X}=\text{BaCuO}_{3-\delta}$. The group X is usually referred to as the ‘charge reservoir’ and the elements A sometimes called the ‘spacer’, or better, ‘intercalant’.[‡]

A description of the structure which is conventional in the literature is the ‘four-number naming scheme’, e.g. ‘2201’: note that this does not identify the composition uniquely. In the 4-number scheme, the last two numbers correspond to $n-1$ and n respectively in the above notation, hence we always have $4 = 3 + 1$. The 2nd number is always 2, and describes the number of so-called ‘spacing’ layers, which always contain O (cf. below). Finally the first number (which may be 0) (cf. below) specifies the number of so-called ‘insulating’ layers, typically a heavy metal oxide (Pb, Bi, Tl, Hg, ...). Thus, e.g., in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the two ‘spacing’ layers are BaO and the ‘insulating’ layer (in this case actually not very insulating!) is the CuO chains, while in La_2CuO_4 the two spacing layers are LaO and there is no ‘insulating’ layer. [Note: do not confuse this naming scheme with ‘214’, ‘1237’ etc.!].

An alternative point of view on the structure, which comes naturally to chemists, is

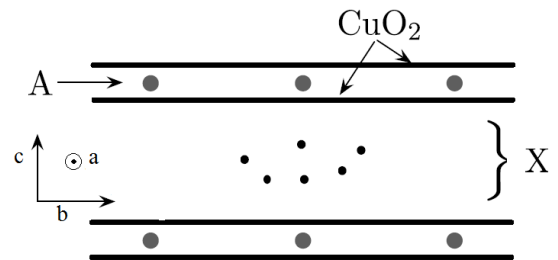


Figure 1:

(Notation: c-axis \perp CuO_2 planes, ab-axes in plane.)

*Statement probably out of date in 2015 (FeSe, H_2S)

[†]Except for the so-called infinite-layer compound where $\text{X} = 0$, see below.

[‡]‘Spacing layer’ is conventionally used in a different sense, see below.

to note that in the case of a single-plane ($n = 1$) material the constitution of the spacing layers relative to the CuO_2 plane is such that each Cu atom is surrounded by six O atoms (4 in the plane, cf. below, and 2 in the neighboring spacing layers) at approximately equal distances, which thereby form an octahedron[‡] (8 sides, 6 vertices!). The out of plane O atoms in the ‘spacing’ layers are conventionally called the ‘apical’ O’s and are often thought to play a significant role in the superconductivity. In a multilayer material the octahedra get as if were elongated.

From a chemical point of view the cuprates are a subclass of the so-called perovskite materials. The original perovskite is CaTiO_3 , and rather generally the formula can be written as ABO_3 , where A is a divalent cation (i.e. the ionization state is ++), and B is an element or complex with charge 4+. In the original perovskites such as CaTiO_3 and SrTiO_3 , which are cubic in structure, the oxygens form an octahedral ‘cage’ around the divalent cations (Ca, Sr ...), and this feature is preserved more generally. In the cuprates the role of A is played by the in-plane Cu atom, which is doubly ionized in the parent state (see below), and that of B by the group X and, if it exists, the element A of our classification.

At this point it is helpful to recall the place of the various elements we shall encounter in the periodic table, and their normal ionization states:

Element	At. number	Configuration	Ionization state	Ionic radius ¹
O	8	$1s^2 2s^2 2p^4$	2-	1.21
Cu^2	29	$\text{Ar} + 3d^{10} 4s$	2+	0.73
Ca	20	$\text{Ar} + 4s^2$	2+	1.12
Sr	38	$\text{Kr} + 5s^2$	2+	1.26
Ba	56	$\text{Xe} + 6s^2$	2+	1.42
La	57	$\text{Xe} + 5d 6s^2$	3+	1.16
Y	39	$\text{Kr} + 4d 5s^2$	3+	1.02
RE's	58-71	$\text{Xe} + \text{various} + 6s^2$	3+	0.97(Lu)-1.14(Ca)

} (intercalant)

The heavy metals Hg, Tl, Pb, Bi ($Z = 80, 81, 82, 83$) have the Xe closed shell $+5d^{10} + 2, 3, 4, 5, 6s/6p$ electrons respectively and prima facie have valence 2, 1 or 3, 2 or 4 and 3 or 5 respectively; however, the question of the valence of these elements in the cuprates is not straightforward, see below.

[‡]Note asymmetry: Cu-O distance = 1.9\AA for in plane O's, 2.4\AA for apicals.

¹From CRC Handbook of Chemistry and Physics, 80th ed. pp. 12, 14-16. The coordination numbers used are $z=2,6,8$, respectively for O, Cu and the rest respectively, corresponding to in-plane positions for O and Cu and intercalant positions for the rest.

²The valence (ionization state) listed is for the Cu's in the CuO_2 planes. Confusingly, the Cu's in the chain in YBCO are thought to be in ionization state 3+.

From the Table one sees that it is often possible to construct, for a given choice of the elements in the ‘charge reservoir’ X, a stoichiometric compound such that the valences balance: e.g. La_2CuO_4 or $\text{YBa}_2\text{Cu}_3\text{O}_6$, (see footnote 2). When one balances the valences in this way, the plane Cu’s (which start with a $3d^{10}4s$ configuration) are left in the $3d^9$ configuration, i.e. with one ‘hole’ per Cu atom in the d -shell. Thus, naive application of band theory would predict that at least the ‘single-layer’ compounds of this class (e.g., La_2CuO_4) would be metals, since they have odd number of electrons per unit cell. In fact, the two stoichiometric compounds above are both antiferromagnetic insulators, and all the evidence is that they are ‘Mott insulators’ (each electron effectively confined to its own unit cell, with AF ordering). Suppose, now, one starts from such a compound (usually called the ‘parent’ compound) and dopes the system by (e.g.) replacing some of the La (valence 3+) with Sr (valence 2+), i.e. making $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [beware differences in notation – see below]. The effect is that an average of x electrons per unit cell are ‘missing’, or equivalently we have x extra holes per unit cell; the general belief is that those holes migrate to the CuO_2 planes, where they sit predominantly on the Cu sites (though cf. below). An alternative way of doping La_2CuO_4 is to keep the La unsubstituted but to vary the number of oxygens away from the stoichiometric value 4, i.e., make it $\text{La}_2\text{CuO}_{4+\delta}$; this should prima facie similarly donate 2δ holes per unit cell to the CuO_2 planes. Oxygen ‘deficiency’ is the most common way of doping YBCO, but in this case the notation may be a little confusing: for historical reason, the normal convention is to write the compound as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, but one must remember that in this case the ‘parent’ compound is actually $\text{YBa}_2\text{Cu}_3\text{O}_6$, so in hindsight, a more natural notation would be $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (or O_{6+x}), with $\delta \rightarrow 1-\delta$, and this is indeed sometimes used. Also, one must remember that in this case, there are 2 CuO_2 planes per formula unit, so if one naively took across the argument used for LSCO one would conclude that for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ the number of holes per (in-plane) CuO_2 unit is δ . Actually, this conclusion is almost certainly misleading, because in this case all the evidence is that for small δ an appreciable fraction of the holes are ‘captured’ by the chain Cu’s, and only when δ exceeds some threshold value of the order of 0.4 do most of the holes start migrating to the planes.

In the case of heavy-metal-containing cuprates such as Tl-2201 or Hg-1201, the stoichiometric compound (e.g., $\text{Tl}_2\text{Sr}_2\text{CuO}_6$) again has one unpaired electron per CuO_2 unit and thus, by analogy with La_2CuO_4 or $\text{YBa}_2\text{Cu}_3\text{O}_6$, might be expected to be a Mott insulator: in fact, however, it is a metal. The reason for this is believed to be that the valence state of the Tl is not in fact 3+; this is confirmed by band structure calculations, which indicate that the band derived from the $6s$ state of Tl overlaps the relevant Cu and O-derived bands. (see below).

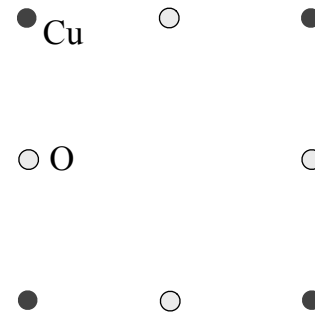
The whole question of the relation of the chemical stoichiometry δ to the number of holes effectively available per (plane) CuO_2 unit is a vexed and much-debated one; I will return to it below in the context of the phase diagram.

However, before leaving the subject of structure there is one further question which needs to be addressed, namely the existence of ‘homologous series’. A homologous series is defined as a series of compounds $(\text{CuO}_2)_n\text{A}_{n-1}\text{X}$ with the same choice of A

and (apart possibly from small differences in the quantity δ) of X but different values of n . Examples are the series $\text{Tl}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ (Tl-2201, 2212, 2223 ...) and $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ (Hg-1201, 1212, 1223 ...); they differ simply in the number of CuO_2 planes per unit cell. A point which is sometimes confusing but follows from simple valence arguments is that since each CuO_2 unit added contributes two holes, if one is giving to stay anywhere near the ‘stoichiometric’ compound (which turns out to be the ‘interesting’ regime in the context of superconductivity) the element A must be an alkaline earth (Ca, Sr, Ba) (or in principle some other divalent cation), not Y or a rare earth. Thus it is no accident that YBCO and its RE substituted-analogs occur only for $n = 2$ and have no homologues.

Crystal structures of the cuprates[¶]

The crystal structures of many of the cuprates have been determined with high accuracy by X-ray analysis. To start with the CuO_2 planes, these are to a first approximation square (usually exactly so in the single-layer cuprates), with the Cu’s sitting on the corners of the square unit cell and the O’s in the ‘side-centered’ position. In most cases the lattice constant^{||} is close to $3.84 - 3.85\text{\AA}$, though a value as small as 3.79\AA is found (for LSCO) and also one as large as 3.95\AA (for NCCO: note that the ‘infinite-layer’ material also has a large value, 3.93\AA). Note that if we use the ‘naive’ tabulated values given in the Table for the ionic radii of Cu^{++} (which we remember is in six-fold coordination because of the apical O’s) and O^{--} (assumed to be in 2-fold coordination) close packing of the spheres along the crystal axes gives a lattice constant of 3.88\AA .



It should be noted that even when not only the CuO_2 plane but the crystal structure as a whole is exactly tetragonal, neighboring planes may be shifted by $(1/2, 1/2)$ relative to one another, so that the true crystallographic unit cell contains two CuO_2 planes. (However, physicists tend to refer loosely to a ‘unit cell’ which is half the true one). In the less symmetric case where the crystallographic symmetry is orthorhombic neighboring CuO_2 planes may also be somewhat twisted relative to one another.

In the case of the bilayer cuprates ($n = 2$), even those with tetragonal crystal symmetry (such as Tl-2212), the CuO_2 planes are almost invariably buckled inwards, i.e. the oxygens in the neighboring bilayers are closer than the Cu’s. The buckling expressed in terms of the Cu–O–Cu bond angle, varies from a maximum of $\sim 166^\circ$ (YBCO 1237) to close to 180° (i.e., almost no buckling) for Hg-1212.

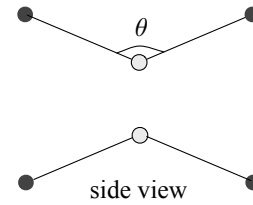
Because of the buckling, the concept of the ‘distance between the planes of a bilayer’ is not exact; however, the average distance is always close to 3.1\AA . This appears to be roughly consistent with close-packing of the O-intercalant-O chain, if one assumes that the effective ionic radius of O^{--} is now a little greater than its coordination-2 value. In general, bilayer cuprates intercalated with Ca tend to be less buckled than those intercalated with Y or a rare earth, whose ions are smaller. In addition to buckling,

[¶]Ref: Shaked et al., op.cit., or for more details Hazen in Ginsberg II.

^{||}In the literature it is sometimes quoted as $\sim 5.3\text{\AA} \approx \sqrt{2} \times 3.84\text{\AA}$ for crystals with orthorhombic symmetry.

which can and does occur even in tetragonal materials, there maybe some degree of orthorhombic asymmetry even within the CuO_2 planes. However, this is usually fairly small; for example, in YBCO the two in-plane crystal lattice constants are 3.82\AA and 3.89\AA respectively, a difference of $< 2\%$, and the difference in the buckling angles is even smaller ($< 0.3\%$).

3-layer cuprates again have a typical intra-trilayer spacing of around 3.1\AA , with the central plane in this case being flat (assuming that the two intercalant atoms are identical which is normally the case*). One can go on increasing the number of layers in some homologous series at least up to $n = 5$, and the general structure stays much the same. Cf. also the ‘infinite-layer’ compound described below.



All cuprates, be they single- or multilayer, have a spacing between neighboring planes or groups of planes (i.e. an ‘effective c -axis cell dimension’) which is larger, often much larger, than the side ($\sim 3.84\text{\AA}$) of the in-plane ‘unit cell’. The spacing in fact typically ranges from about 6 to 15\AA . Since in addition much of the inter-plane material is fairly insulating while the CuO_2 planes are conducting, this means that the cuprates are strongly anisotropic in almost all their properties: crudely speaking, it seems consistent to assume that the ‘ ab -plane’ properties are mostly determined by the behavior of the electron (holes) in the CuO_2 planes, and it is thus not surprising that they show, at least qualitatively, a fair degree of universality (see lecture 5); on the other hand one would expect that most of the c -axis properties would be sensitive to the inter-multilayer materials and would thus tend to be material-specific – again as found experimentally.

Band structure: It is not entirely clear how useful are detailed band structure calculations for the cuprates, since interactions between the conduction electrons are believed to be strong (cf. the Mott-insulator nature of the parent state). However, one conclusion which seems fairly robust is that the main bands associated with the CuO_2 planes which are likely to play a role in the low-energy properties are those derived from the $2p_{x,y}$ states of the oxygens and the $3d_{x^2-y^2}$ states of the Cu’s (the $3d_{z^2}$ states of the latter may also play some role). There is thought to be fair degree of $\text{O}(2p)$ – $\text{Cu}(3d)$ hybridization. In compounds such as LSCO these are likely to be the only relevant bands: in heavy-metal compounds such as Tl-2201 the Tl $6s$ band may also lie at relevant energies, but the degree of hybridization is not thought to be great, i.e. the $(2p)$ – $(3d)$ states are largely localized in the CuO_2 planes and the $6s$ ones largely in the TlO planes.

Some cuprates of special interest:

- (1) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (‘LSCO’, ‘214’): $n = 1$, $X = \text{La}_2\text{O}_2$. Structure: 0201, tetragonal/orthorhombic: $T_c < 50\text{K}$ ($\text{O}_{4+\delta}$).

A very early discovery (immediately after the original BM compound $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$). Sr can be substituted by O surplus, i.e., $\text{La}_2\text{CuO}_{4+\delta}$. Very large and fairly pure crystals can be prepared by floating-zone method \Rightarrow very suitable for e.g. neutron

*An exception is $\text{PbBaYSrCu}_3\text{O}_8$, for which one pair of layers is spaced by Y and the other by Sr.

diffraction work.

The bilayer homologues of this material are particularly interesting, see lecture 6.

- (2) $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ ('YBCO', '123'): $n = 2$, $A=Y$, $X=\text{Ba}_2\text{CuO}_{2+\delta}$. Structure: 1212, orthorhombic. Planes strongly buckled. The two BaO 'spacing' layers are more or less independent of δ ; the CuO_x 'layer' is actually a set of chains (conventionally along b-axis), which are complete only for $\delta = 1$. $T_c \leq 92\text{K}$ (note max. reached for $\delta \sim 0.95$ not $\delta = 1!$). Y can be substituted by any RE.[†]

The first real 'high-temperature' superconductor ($T_c > 77\text{K}$). Can be made in reasonably large crystals and fairly pure, hence, 'E Coli' of cuprates. Note no $n \neq 2$ homologues! Some RE analogs (e.g. $\text{GdBa}_2\text{Cu}_3\text{O}_{6+\delta}$) show weak ferromagnetism ($T_M \sim 1\text{K}$), coexisting with SC.

- (3) $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+2)+\delta}$ ('BSCCO'): $n = 1, 2, 3, 4 \dots$, $A = \text{Ca}$, $X = \text{Bi}_2\text{Sr}_2\text{O}_{4+\delta}$. $T_c \sim 110\text{K}$ ($n = 3$). Structure: $22 \times n - 1 \times n$, tetragonal to a first approximation (but exists a rather long-range 'shearing' (orthorhombic) distribution of CuO_2 planes). Usually occurs in 'flakes' ('like baklava'), hence very well suited to transmission experiments (optics, EELS etc.) and also to ARPES (but note almost always cleaves along BiO planes, hence have to 'burrow down' 2 layers to see CuO_2 planes).

Note that in this series (as also in Tl-1201) the $n = 1$ member has a fairly low T_c (never more than $\sim 30\text{K}$ in existing experiments) while the higher members have respectable ones ($\sim 90\text{K}$ for $n = 2$, $\sim 110\text{K}$ for $n = 3$).

The Bi series are probably the most anisotropic of the known cuprates, with a intermultilayer spacing of $\sim 15\text{\AA}$. This is reflected in the extreme anisotropy of the resistivity ($\sim 10^5$, see lecture 5).

Note $n = 2$ member recently made with complete $\text{Ca} \rightarrow \text{Sr}$ substitution.

- (4) $\text{Tl}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+2)+\delta}$ ('TBCCO'). $A = \text{Ca}$, $X = \text{Tl}_2\text{Sr}_2\text{O}_4$, structure as Bi series, but no 'superlattice', in fact CuO_2 planes very close to square. $T_c \sim 95\text{K}$ even for $n = 1$, can be made fairly pure + fairly large crystals (not 'flaky'). Can be 'overdoped', i.e., $\delta >$ value corresponding to max. of T_c (close to $\delta = 0$).

Drawback: probably most toxic of known cuprates! Exists also Tl- $12n-1n$, qualitatively similar to Bi series.

- (5) $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)}$ ('HgBCO'): $A = \text{Ca}$, $X = \text{HgBa}_2\text{O}_2$. Note, in distinction to Tl series, Hg forms non-oxide layer.[¶] $n = 1$ member under pressure of 20 GPa has highest known T_c for one-layer material (120K): $n = 3$ at 20 GPa is world record holder at T_c (onset) $\sim 160\text{K}$. Note the 'Hg-free Hg' compound ($\text{Hg} \rightarrow \text{Ca}$).

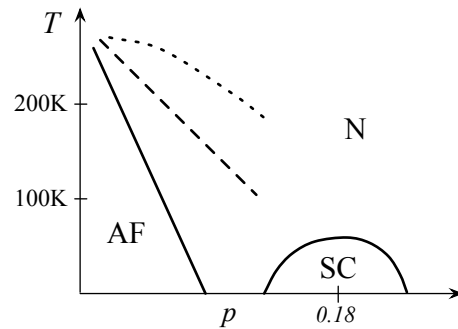
[†]The situation regarding the superconductivity or not of $\text{PrBa}_2\text{Cu}_3\text{O}_{6+\delta}$ appears to be complicated.

[¶]It is actually a bit more complicated than this: the O site in the Hg layer is partially occupied, see Shaked et al. p. 26.

- (6) $\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_4$ ('NCCO'): $n = 1$, $X = (\text{NdCe})_2\text{O}_2$. $T_c \lesssim 35\text{K}$. The most interesting feature of this compound is the nature of the in-plane doping. The RE Nd has a fairly stable valence of 3+, so the $x = 0$ 'parent' state is expected to be a Mott insulator as usual. However, Ce is 'mixed-valence': (cf. its role in the HF compounds): the 4+ state is also possible. Apparently, the extra electrons ($\leq x$) made available migrate into CuO_2 planes. Thus NCCO is often called an 'electron-doped' material, in contrast to most of the other cuprates which are 'hole-doped'.
- (7) $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$ ('infinite-layer'). This compound is unique in that the 'reservoir' group X is nonexistent: we have simply an infinite set of CuO_2 planes separated by the AE ions Ca or Sr. T_c can range up to $\sim 110\text{K}$, but it is often not clear whether the material is single-phase. (and the chemistry of the doping is not immediately clear, since Ca and Sr are isovalent): however, it is usually regarded as a hole-doped material, see Shaked et al. p. 70.

The phase diagram*

Construction of a generic phase diagram for the cuprates requires a certain act of faith: namely, that what controls the 'interesting' behavior is the number of carriers p in the CuO_2 plane, i.e. the number of holes per CuO_2 unit over and above the value (namely 1) for the stoichiometric 'parent' compound (La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_6$, etc.): and moreover that we can make a reasonable guess at the relation between p and the chemical stoichiometry. For example, in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ it seems reasonable, *prima facie*, to take $p = x$, while for $\text{La}_2\text{CuO}_{4+\delta}$ we would expect $p = 2\delta$. For compounds such as $\text{Tl}_2\text{Sr}_2\text{CuO}_{6+\delta}$, we have no a priori knowledge (other than, possibly, BS calculations) as to the value δ_0 of δ which corresponds to the 'parent' compounds, but we can say that a change $\Delta\delta$ in δ corresponds to a change $\Delta p = 2\Delta\delta$ in p . It then makes some sense to ask if with an appropriate choice for δ_0 the phase diagram of Tl-2201 is reasonably similar to that of LSCO and YBCO in the range of p where it overlaps with them, and if so to adopt this choice of δ_0 . In this way, we obtain the schematic phase diagram shown in the figure: note carefully that any given compound will usually correspond only to a finite range of p -values. The dotted line corresponds to a gradual crossover from (strange-) metallic to (spin-glass) insulating behavior, the nature of which is not entirely clear (in particular, it does not seem clear at present whether there is a genuine phase transition or not; but cf. lecture 6). The dashed line which corresponds to a relatively well-defined crossover (see lecture 6) is sometimes called $T^*(p)$. Note that the 'height' of the SC region (i.e., T_c^{max}) varies a lot from compound to compound, but typically is of order 100K. Note $n \approx 1.5 \times 10^{14} \text{cm}^{-2}$ for $p = 0.18$. Hence $n_{3D} \sim 1 - 2 \times 10^{21} \text{cm}^{-3}$.



*This discussion is very preliminary: we return to the details of the phase diagram in l. 6.