Preparation and Characterization of *Real* Materials
A CCMS Summer Lecture Series
July 21 – August 1, 2008

Acknowledgements: Parts of these lectures were given at Seoul National University the week of July 7, 2008. Work at University of Florida performed under the auspices of the US Dept. of Energy, contract no. DE-FG02-86ER45268. I have attempted to give proper citations on each slide – for where these are lacking, please consult the author – G. R. Stewart.
Preparation and Characterization of Real Materials
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0-d (small – a few 100 Å - particles, molecular magnets)
1-d (carbon nanotubes/polymers/below a dimensionality transition)
2-d (films, 3-d systems with strong anisotropy)
3-d (the rest)
Examples of 1-d Materials Prep.  
Univ. of Florida

1D coordination polymer:
\[ [\text{Me}_4\text{N}]_3\{[\text{Mn}(5-\text{MeO-salen})][\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]\} \]

*Chem. Mater.* 2007, 19, 2238-2246

Zhou, et al. (Kevin Little, Dan Pajerowski, Mark Meisel – Physics U of F; Dan Talham – Chemistry U of F)
Examples of 1-d Materials
Prep./Characterized Univ. of Florida

- (CH$_3$)$_2$NH$_2$CuCl$_3$, referred to as MCCL, a system of one-dimensional chains of copper spins (Meisel/Talham)

- Low-dimensional (quasi 1-d) charge-transfer salts (EDO-TTF)$_{2X}$ (X=PF$_6$ and AsF$_6$) (Tanner group)

- Quasi 1-d organic superconductors (Hill group), antiferromagnets (Ba$_3$Mn$_2$O$_8$-Andraka/Takano)
Single-Walled Carbon Nanotubes (Lecture July 25 by A. Rinzler)
Zhizhong Chen, Xu Du, Mao-Hua Du, C. Daniel Rancken, Hai-Ping Cheng, and Andrew G. Rinzler (Physics – U of F)
2-d

- Thin films of Fe – the “Quantum Dance”
  - measurements on ultrathin ( < 100 Å thick) Fe films (Hebard group)

- In 2-d, when the thickness falls to a certain value (e.g. 50 nm), the dc electrical conductivity has a peak as a function of thickness due to higher carrier mobility. Higher mobility is expected in one dimensional confined paths where transverse scattering is reduced thus improving the mean free path of the carriers.

- Quasi 2-d hi-$T_c$ superconductors like BiSCO
2-d character in $\text{hi-}T_c$

$\text{Y Ba}_2\text{Cu}_3\text{O}_7$

Cu Oxide planes
3-d

- Much work is still in 3-d; even a thin film is 3-dimensional as long as the thickness > mean free path/coherence length. Contrary wise, a 3-d material made small → 0-d
- Also, many "quasi – 2d" materials have anisotropies that are < 10.
- hole-doped perovskite manganites $RE_{1-x}Ca/Sr_xMnO_3$ (Biswas) in film form
$^3\text{He}$ and $^4\text{He}$, solid $\text{H}_2$

- $^3\text{He}$ in aerogel: effects on the superfluid ($p$-wave) condensate of disorder/restricted dimension (Yoonseok Lee group)
- Solid $\text{H}_2$ – NMR in Sullivan group
Compositional purity and sub-lattice disorder are very often critical.

Examples:

- High vacuum needed to prevent oxidation of the thin Fe film.
- In flux growth of single crystals, the flux is the obvious candidate for impurities "see next slide"
Superconducting Transition Width in flux-grown vs arc-melted $\text{UBe}_13$

Data from H. R. Ott, et al.
The moral of the story – just because it’s a “single crystal” doesn’t mean it’s perfect!
Beware Hazards of Samples

- Superconducting Hi-T_c Tl compound ("superconducting rat poison")
- Asbestos like hazard in carbon nanotubes: "researchers observed that longer nanotubes behaved like asbestos, provoking inflammation and lesions in mice." Associated Press May 20 reporting on article in Nature. Nanotechnology nanotubes are already used in some products, like tennis rackets, golf clubs or bicycle frames, researchers say that the fibers appear to pose little risk to consumers.
- The new ‘high’ T_c Arsenic-containing compounds
- Or, you can work really hard – e. g. OsO_4 is very toxic but only forms in the bulk above 670 K.
I. Always check for **hazardous** properties of the materials/processes being used for a sample ‘new’ to you.

II. Just because some element is harmless in its bulk form does **not** mean that in, e.g., the powdered form that it continues to be harmless. (simple example, flammability.)
III. Mixtures of ~ harmless components can be very dangerous (Se + acid → H$_2$Se)

4 = Very short exposure could cause death or major residual injury (H$_2$Se exposure limit: 0.3 ppm over an 8 hour period vs 140 ppm for HCN.)

4 = will burn readily. Flash point below 23°C
Addition of alcohols to highly concentrated hydrogen peroxide forms powerful explosives.
(Brief) History of Sample Prep

- Gold is found as a free element (i.e. not a compound) in nature and is associated with quartz, pyrite and other minerals. Gold has been known since ~ 6000 BC.

- To extract gold from pyrite compounds, they are sometimes treated in a proprietary chlorine process. The roasted pyrites are moistened with water and impregnated with chlorine gas. Gold chloride is then leached out with water, and the gold is precipitated by reduction with ferrous sulfate or solid charcoal. Bromine water is sometimes used instead of chlorine. The gold obtained is then processed into bullion. The gold bullion is then refined. If the gold contains copper, it is removed by oxidizing it with borax and nitric acid. (Also cyanide leaching, mercury amalgamation) (http://www.newton.dep.anl.gov/askasci/gen01/gen01415.htm)

* Ag is etched out of ‘granulated’ Au – achieved by putting molten gold into cold water – via HNO₃ (starting in the 1200’s)
Removal of noble metal Pt from Au (discovered by the Spanish in the 1500’s Pt was considered a worthless impurity in Au). Thus, purity has long played a role.
Purities of the Elements (a quick look)

- NIST gold is 99.9999%+
- Ge after zone refining, $1/10^{10}$ impurity
- $^3$He can have better than $1/10^{50}$ purity – Yoonseok Lee
First metal alloy:
Bronze (88%Cu,12%Sn) – 4000 BC

- Bronze was replaced by Iron implements only after Steel (Fe alloyed with 0.2-2 wt% or 1-10 at% C) was invented ~ 1400 BC

- Iron is extracted from Fe$_2$O$_3$ by removing the oxygen by combining it with a preferred chemical partner such as carbon. This process, known as smelting, was first applied to metals with lower T$_{melt}$ like Cu (~1000 °C), Sn (250 °C). Cast iron—iron alloyed with greater than 1.7% carbon—melts at around 1370 °C. All of these temperatures could be reached with ancient methods that have been used for at least 6000 years. Since the oxidation rate itself increases rapidly beyond 800 °C, it is important that smelting take place in a low-oxygen environment. Unlike copper and tin, liquid iron dissolves carbon quite readily, so that smelting results in an alloy containing too much carbon to be called steel. (Wikipedia)
The maximum solubility of carbon in iron (in austenite) is 2.14 wt % at 1149 °C.
Carbon and other elements (Cr, Mn, V) act as a hardening agent, preventing dislocations in the iron atom crystal lattice from sliding past one another.

The heat treatment process for most steels involves heating the alloy until austenite forms, then quenching the hot metal in water or oil, cooling it so rapidly that the transformation to ferrite (α-Fe) or pearlite does not have time to take place.

Cementite forms in regions of higher carbon content while other areas revert to ferrite around it. Self-reinforcing patterns often emerge during this process, leading to a patterned layering known as pearlite (Fe₃C:6.33Fe) due to its pearl-like appearance. (http://en.wikipedia.org/wiki/Steel)
assumed for the present that any pearlite which is not distinctly lamellar is not true pearlite.

It will be noted that in Figure 2 the pearlite occupies about twice the area covered by the same constituent in Figure 1. We infer from this that the amount of pearlite in low carbon steel at least increases progressively with the carbon content. Doubling the amount of carbon doubles of course the proportion of the iron carbide in the steel, and since the amount of pearlite is apparently also doubled it follows that iron carbide and ferrite must unite with each other in fixed ratio to form pearlite, in other words that pearlite always contains the same proportion of carbide and hence also of carbon. The accuracy of this conclusion will soon be shown.

**Free Ferrite.** — To distinguish between the ferrite included in pearlite and the ferrite forming the balance of low carbon steel, the latter is sometimes called “free”
What happens to an X-ray pattern when a cubic system (e.g. fcc Austenite Fe-C steel) undergoes a tetragonal distortion (to bct Martensite)?
Martensite, named after the German metallurgist Adolf Martens (1850-1914), is any crystal structure that is formed by displacive transformation, as opposed to much slower diffusive transformations. "Martensite" most commonly refers to a very hard form of steel crystalline structure (the alloy of iron and carbon) important in some tool steels. The bct martensite is formed by rapid cooling (quenching) of fcc austenite which traps carbon atoms that do not have time to diffuse out of the crystal structure. Thus, the phase that should form (Fe₃C) is suppressed and a structure not shown in the binary phase diagram (which depicts thermodynamic equilibrium) is produced.
Example of Martensitic Transformation: A-15 (cubic) $V_3Si \rightarrow$ tetragonal $V_3Si$

$T_m = 21.2 \text{ K}$

G. R. Stewart, et al.
The effect of this ‘martensitic’ transformation on $V_3Si$, its superconductivity, the lattice softening in the elastic constants in the $c$-axis direction ($c_{44}$ and $c_{66}$ have to $\to 0$ at the transformation) has been extensively studied.
Remember, this kind of transformation can be metastable.

FIG. 3. Zero-field (circles) and 18-T (diamonds: below 7 K, field is 19 T) specific-heat data for nontransforming V₃Si. The
Phase Diagrams—We’ve seen the one below for Fe-C, what about another one to analyze?

The maximum solubility of carbon in iron (in austenite) is 2.14 wt % at 1149 °C.
This 63-37 composition is also known as the eutectic point of the alloy, where the alloy behaves like a pure metal having a single melting (solidification) temperature (176°C / 349°F). This is a good operational feature. Once the solder melts on application of heat, it solidifies immediately on removal of heat, without going through a pasty stage like other alloys. This allows for predictable soldering and fast cycle times.
Properties at room T depend on cooling rate!
Phase Diagram #3 Copper-Zinc (Brass)

- ‘cartridge’ brass
- ‘Muntz’ or ‘α-β’ brass
- ‘brazing’ solder

Properties at room T depend on cooling rate!

(rhombohedral hexagonal)

Zn (%)

T (°C)
Phase Diagram #4: Copper-Gold

Massalski, ASM binary phase diagrams
Phase Diagram #4: Copper-Gold

The occurrence of compound-like phases at the AuCu and the AuCu$_3$ stoichiometric compositions was first observed by [15Kur], who employed thermal analysis, hardness, and X-ray measurements. [23Bail], [23Bai2], and [23Bai3] associated the occurrence of atomic ordering with these compounds on the basis of observed X-ray diffraction lines. [36Joh] discovered an additional order-order transformation in AuCu at higher temperatures, in which an orthorhombic AuCu(II) phase forms from the tetragonal AuCu(I) phase. Prior to this, AuCu(I) was thought to transform directly to the disordered fcc phase (AuCu(D)) at higher temperatures.
Phase Diagram #5: The Actinides

J. L. Smith
Sample Prep-an Example

- A practical example of sample prep from new work on making the iron arsenide superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ from Sn flux growth. Advantages: get single crystals for the first time of these new FeAs ‘high $T_c$’ superconductors; avoid somewhat the vapor pressure problems of K and As ($P_{\text{vapor}} = 10$ mm at 443 and 437 °C respectively).

- Reference: “Anisotropic thermodynamic and transport properties of single crystalline $(\text{Ba}^{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ ($x = 0$ and 0.45)”. by N. Ni, S. L. Bud’ko, A. Kreyssig, S. Nandi, G. E. Rustan, A. I. Goldman, S. Gupta, J. D. Corbett, A. Kracher, and P. C. Canfield

arXiv:0806.1874v1
First thing to do: look at binary phase diagrams between Ba, K, Fe, As and Sn.

Note the good solubility of Ba in Sn at relatively low (~ 400 °C) temp.
First thing to do: look at binary phase diagrams between Ba, K, Fe, As and Sn

Note the ok solubility of K in Sn at relatively low temp.
First thing to do: look at binary phase diagrams between Ba, K, Fe, As and Sn

Note the poor solubility of Fe in Sn at low temp., need 800 °C
First thing to do: look at binary phase diagrams between Ba, K, Fe, As and Sn

Massalski, binary phase diagrams, ASM

Note the good solubility of As in Sn at low temp.
Why was Sn chosen instead of Cu, Cd, Al, Ga, In, Pb, Sb, Bi, ...?

- In order to answer this, would need to go look at the binary phase diagrams between Ba, K, Fe, As and each of these other possible fluxes (all of which are in common use for preparation of various single crystals.) Another consideration is the ease of removing the metal flux ($T_{\text{melt}}$).

Let’s go look!
Characterization

- See, e.g., Prof. Biswas’s site
- [http://www.phys.ufl.edu/nanofab/equipment.html](http://www.phys.ufl.edu/nanofab/equipment.html)
- [http://maic.mse.ufl.edu/](http://maic.mse.ufl.edu/)

Outline:

I. via X-rays
II. via electron microprobe
III. via SEM
Short Overview of Sample Characterization by
I. X-ray Diffractometry

- Various resources for this:
  - http://www.phys.ufl.edu/courses/phy4803L/group_I/x_ray/xray.pdf
  - C. Kittel, *Introduction to Solid State Physics*
  - B. D. Cullity, *Elements of Xray Diffraction*
Sketch of Bragg Reflection of Incident Radiation of Wavelength $\lambda$

\[ n\lambda = 2d \sin \Theta \] (eq. 1)
Diffraction from various crystal planes

The spacings for all possible lattice planes in the sc lattice can be represented by

\[ d(hkl) = \frac{n a_0}{(h^2 + k^2 + l^2)^{1/2}} \]

where \( hkl \) are integers \{called the Miller indices\} and \( n \) is an integer. Together with eq. 1

this leads to

\[ \lambda = \frac{2a_0 \sin \Theta}{(h^2 + k^2 + l^2)^{1/2}} \]

where \( a_0 \) is the length of the cube edge.
Diffraction from various crystal planes; Miller indices

In cubic crystals, the direction \([hkl]\) is \(\perp\) to a plane with Miller indices \((hkl)\).

Specify the orientation of a plane by the indices determined via:

1. Find the intercepts on the axes in terms of the lattice constants \(a_1, a_2, a_3\).
2. Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest 3 integers. The resulting Miller indices \((hkl)\) are called the index of the plane.

<table>
<thead>
<tr>
<th>X-ray Diffraction and Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diagram of crystal lattices" /></td>
</tr>
</tbody>
</table>

\(\infty, 1, \infty \rightarrow (0,1,0)\)  
\(1,1, \infty \rightarrow (1,1,0)\)  
\(2,1, \infty \rightarrow 1/2,1,0 \rightarrow (1,2,0)\)

Top view of three possible sets of planes in the simple cubic lattice with their Miller indices.
The (100) plane

The (111) plane

The (101) plane

The (110) plane, origin moved to the right.
A crystal structure is described by a lattice, e.g. a simple cubic lattice:

plus a set of atoms (called the ‘basis’) attached to each lattice point. Thus, for a bcc lattice, the basis is two atoms, one at 0,0,0 and one at \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) \((u_j, v_j, w_j)\). A crystal thus consists of a basis of atoms at each lattice point. This can be expressed: 

\[ \text{lattice} + \text{basis} = \text{crystal} \]
X-ray Crystallography

The Bravais Lattice Types

CUBIC
\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

TETRAHEDRAL
\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

ORTHORHOMBIC
\[ a \neq b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

HEXAGONAL
\[ a = b = c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

MONOCLINIC
\[ a \neq b \neq c \]
\[ \alpha = \gamma = 90^\circ \]
\[ \beta \neq 120^\circ \]

TRICLINIC
\[ a \neq b \neq c \]
\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

4 Types of Unit Cell
- P = Primitive
- I = Body-Centred
- F = Face-Centred
- C = Side-Centred

7 Crystal Classes → 14 Bravais Lattices
(Bravais lattice) AND INTERAXIAL ANGLES

**CUBIC** three equal axes, Au, Cu, NaCl, Si, GaAs
(Simple cubic, three right angles
Body-centered cubic, \(a = b = c, \alpha = \beta = \gamma = 90^\circ\)
Face-centered cubic)

**TETRAGONAL** Two of the three axes equal, In, TiO\(_2\)
(Simple tetragonal, three right angles
Body centered tetragonal) \(a = b \neq c, \alpha = \beta = \gamma = 90^\circ\)

**ORTHORHOMBIC** Three unequal axes, Ga, Fe\(_3\)C
(Simple orthorhombic, three right angles
Body centered orthorhombic, \(a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ\)
Base-centered orthorhombic,
Face-centered orthorhombic)

**RHOMBOHEDRAL** Three equal axes equally inclined, Hg, Bi
(Simple rhombohedral) three equal angles \(\neq 90\)
\(a = b = c, \alpha = \beta = \gamma\)

**HEXAGONAL** Two equal axes at \(120^\circ\), Zn, Mg
(Simple hexagonal) third axis at right angles
\(a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ\)

**MONOCLINIC** Three unequal axes, KClO\(_3\)
(Simple monoclinic, one pair of axes not at \(90^\circ\)
Base- centered monoclinic) \(a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ\)

**TRICLINIC** Three unequal axes, Al\(_2\)SiO\(_5\)
three unequal angles
\(a \neq b \neq c, \alpha \neq \beta \neq \gamma\)
Not all reflections are of equal intensity. As \( hkl \) get large, the density of atoms in each plane decreases and the corresponding peak gets weaker.

Top view of three possible sets of planes in the simple cubic lattice with their Miller indices.
Because of the $j$ scattering sites within each cell, the intensity of the peak will be proportional to the square of the magnitude of the \textit{crystal structure factor}

\[ F(hkl) = \sum_j f_j \exp\left\{2\pi i(hu_j + kv_j + lw_j)\right\} \]

The \textit{atomic form factor} $f_j$ above depends on the type of atom at the site $u_j$, $v_j$, $w_j$. It also varies with $\Theta$. For $\Theta = 0$, it is approximately proportional to the number of electrons in the atom. For larger reflection angles, it decreases due to inter-ference effects of scattering from different parts of the atom.
Consider a body-centered cubic crystal with a two atom basis. Using the sc unit cell, we would have to include one atom at the sc lattice site (0, 0, 0) and an identical atom at the body-centered site (½, ½, ½). The crystal structure factor \( \Sigma_j f_j \exp\{2\pi i(hu_j + kv_j + lw_j)\} \) becomes:

\[ F_{\text{bcc}}(hkl) = f(1 + \exp\{i\pi(h + k + l)\}) \]

This shows that the crystal structure factor for the bcc lattice is non-zero (and equals 2\(f\)) only if \(h + k + l\) is even. Thus peaks with \(h + k + l\) odd would be entirely missing.
If have a bcc (only \(h + k + l = \text{even}\)) lattice, then first lines are (110), (200), (211), (220), (310), (222), (321), (400),

So the ratio of \(\frac{\sin^2 \Theta_n}{\sin^2 \Theta_1}\) values would be the ratio of the successive \(h^2 + k^2 + l^2\) values to the lowest angle \(h^2 + k^2 + l^2\) value (e.g. \(\frac{2^2}{(1^2 + 1^2)} = 2, \frac{2^2 + 1^2 + 1^2}{(1^2 + 1^2)} = 3\), etc.

to give \(2, 3, 4, 5, 6, \ldots\)

Thus, if you are xraying an unknown compound, and you detect this relationship between the \(\sin^2 \Theta\) values for the diffraction pattern, you can conclude that you have a bcc lattice (see discussion of fcc following).
Consider next a fcc cubic crystal with a four atom basis. Using the sc unit cell we would have to include one atom at the sc lattice site $0, 0, 0$ and identical atoms at the face-centered sites $0, \frac{1}{2}, \frac{1}{2}$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, 0)$. The crystal structure factor becomes:

$$F_{fcc}(hkl) =
\begin{align*}
&f \left( 1 + \exp\{i\pi(k + l)\} + \exp\{i\pi(h + l)\} + \exp\{i\pi(h + k)\} \right) \\
\end{align*}$$

This shows that the crystal structure factor for the fcc lattice is non-zero (and equals $4f$) only if the $h, k, l$ are all even or all odd (i.e., unlike the bcc case this is not a restriction on the sum of $h + k + l$, but on the values themselves.)

*Try it and see!*
If have fcc ⇒ hkl are either all even or all odd, so can have (111), (200) {all the permutations like (020) have the same diffraction angle, i. e. they all lie atop one another}, (220), (311), (222), (400), (331), (420), . . . . where these hkl are ordered by the lowest size of $h^2 + k^2 + l^2$ first, therefore (111) is a lower angle xray line than (200), similarly (311) is lower than (222).

Now take $\sin^2 \Theta = (\lambda / 2a_0)^2 (h^2 + k^2 + l^2)$ for the measured lines, So the ratio of successive $\sin^2 \Theta_n / \sin^2 \Theta_1$ values would be $4/3$ ($= 2^2 / (1^2 + 1^2 + 1^2)$), $8/3$ ($= (2^2 + 2^2) / (1^2 + 1^2 + 1^2)$), $11/3$, $12/3 = 4$, etc.
## Selection rules for the Miller indices

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Example compounds</th>
<th>Allowed reflections</th>
<th>Forbidden reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic</td>
<td>Simple cubic</td>
<td>Any ( h, k, l )</td>
<td>None</td>
</tr>
<tr>
<td>Body-centered cubic</td>
<td>Body-centered cubic (e. g. Mo)</td>
<td>( h + k + l ) even</td>
<td>( h + k + l ) odd</td>
</tr>
<tr>
<td>Face-centered cubic</td>
<td>Gold, NaCl, Zinc blende</td>
<td>( h, k, l ) all odd or all even</td>
<td>( h, k, l ) mixed odd and even</td>
</tr>
<tr>
<td>Diamond F.C.C.</td>
<td>Diamond, Si, Ge</td>
<td>all: odd, or even &amp; ( h+k+l = 4n )</td>
<td>above, or even &amp; ( h+k+l = 4n )</td>
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<tr>
<td>Triangular lattice</td>
<td>Hexagonal close packed</td>
<td>( l ) even, ( h + 2k \not\equiv 3n )</td>
<td>( h + 2k = 3n ) for odd ( l )</td>
</tr>
</tbody>
</table>

Flux Growth Single Crystals
Flux Growth Single Crystals – in the Oven

Work at Seoul National University by Yoonseok Oh, et al.
In light of these restrictions, we can create a table of allowed $h^2+k^2+l^2$ combinations (which will be proportional to allowed $\sin^2\theta$ values).

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<table>
<thead>
<tr>
<th>$h^2+k^2+l^2$</th>
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Table 1: Allowed $h^2+k^2+l^2$ combinations for cubic lattices.

Note the interesting arithmetic fact that you cannot get the sum of three integers $h^2+k^2+l^2$ to equal 7, 15, 23 ... - see the simple cubic (sc) case.

Example of x-ray (Cu)
Example of x-ray (Cu)

- Powder diffraction pattern for copper metal shows reflections at $2\Theta = 43.35^\circ, 50.50^\circ, 74.20^\circ, 90.00^\circ, 95.25^\circ, 117.05^\circ, 136.50^\circ, 137.20^\circ, 144.70^\circ$ and $145.70^\circ$. For this pattern, CuK$\alpha$-radiation was used ($\lambda = 1.54178 \text{ Å}$). (When we get to the answer, the lattice constant of copper is known to lie around 3.6 Å).

- Calculate the corresponding values of $\sin^2 \Theta$: $0.136413, 0.181961, 0.3638599, 0.5, 0.545751, 0.727384, 0.862687, 0.866865, 0.908069, 0.913049$

- Now, calculate the ratios of these values to the first value, $\sin^2 \Theta_1$: $0.181961/0.136413 \approx 4/3 (1.3330), 8/3 (2.6673), 11/3 (3.6653), 4 (4.0007), 16/3 (5.3322), \ldots$

so this ratio of successive $\sin^2 \Theta$ (proportional to $(h^2 + k^2 + l^2)$) tells us (without benefit of knowing $a_0$) that Cu has the fcc structure with (calculated from each line) $a_0 = \lambda (h^2 + k^2 + l^2)^{1/2}/(2\sin \Theta) = 3.6151 \text{ Å}, 3.6144 \text{ Å}, 3.6147 \text{ Å}, 3.6158 \text{ Å}, \ldots$. Systematic errors are smaller as $\Theta \rightarrow 90^\circ$ Nelson Reilley extrapolation function, see: http://www.iucr.org/iucr-top/comm/cteach/pamphlets/16/node8.html
‘Mystery’ xray

\[ 2\theta = 38.3^\circ \quad 2\theta = 44.4^\circ \quad 2\theta = 64.9^\circ \quad 2\theta = 77.6^\circ \quad 2\theta = 81.7^\circ \quad 2\theta = 98.1^\circ \quad 2\theta = 111.1^\circ \quad 2\theta = 115.4^\circ \quad 2\theta = 136^\circ \]

Calculate as an exercise whether this is bcc or fcc and what the lattice parameter is. Assume \( \lambda = 1.5418 \text{ Å} \)
Calculate $\sin^2 \Theta$ values:

0.1076118, 0.1427637, 0.28790029

0.39263234, 0.4278219, 0.57045062,

0.6799984, 0.71446757, 0.859670

Calculate ratio of these values to the first one:

1.327 (~4/3), 2.675 (~8/3), 3.649 (~11/3), ...

(errors here are due to my inaccurate reading of a published xray pattern.)

$a_0 = 4.070 \, \text{Å}, 4.081 \, \text{Å}, 4.064 \, \text{Å}, 4.081 \, \text{Å}, ...

4.075 \, \text{Å}, 4.079 \, \text{Å}, 4.073 \, \text{Å} (note how the error in reading the angle $\Theta$ at higher angles has a decreasing effect on the scatter in $a_0$ - $\sin \Theta$ becomes flat vs $\Theta$) (Au is fcc, $a_0 = 4.0782 \, \text{Å}$)
Comparison of Au and Cu xray (Cu xray compressed to overlay the Au at low angles)
How does a bcc xray look?

Note that, as discussed, h+k+l is always even and that $h^2+k^2+l^2$ (2,4,6,8,10,12,... for the lines shown) is both proportional to $\sin^2\Theta$ and evenly spaced. So the appearance of the diffraction pattern is like a ‘fingerprint’ for the structure. For bcc, the evenly spaced $\sin^2\Theta$ corresponds to a gradual progression in $\Theta$.

http://www.eng.uc.edu
In light of these restrictions, we can create a table of allowed $h^2+k^2+l^2$ combinations (which will be proportional to allowed $\sin^2 \theta$ values).

\begin{table}[h]
\centering
\begin{tabular}{c|cccccccccccccccccccc}
\hline
\hline
\end{tabular}
\caption{Allowed $h^2+k^2+l^2$ combinations for cubic lattices.}
\end{table}

**Diamond** (two inter-penetrating fcc lattices) $h^2+k^2+l^2=3,8,11,16$

Other lattice symmetries and hkl

- **Tetragonal:** \( \frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \)

- **Hexagonal:** \( \frac{1}{d^2} = \frac{(4/3)(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \)
Materials Science and Engineering
Research Centers
Major Analytical Instrumentation Center

XRD Philips APD 3720
MAIC Room 117

XRD Philips APD 3720
MAIC Room 117

Philips High Temperature XRD
MAIC Room 107F
SEM example-small particles trapped on a filter
An electron microprobe (EMP), also known as an electron probe microanalyser (EPMA) is an analytical tool used to non-destructively determine the chemical composition of small volumes of solid materials. It works similarly to a scanning electron microscope, in which the sample is bombarded with an electron beam and the resulting excited core electron x-rays that come from the sample are collected. This enables the elements over the beam diameter (~ 1 μ) to be quantitatively analysed at levels as low as 100 ppm.

This is done in MAIC with a EPMA JEOL SUPERPROBE 733

wikipedia
Example of Electron Microprobe Analysis of a Sample

- In CePt$_3$Si, which is superconducting at $T_c = 0.7$ K, sometimes a second transition was seen in the specific heat. Annealing increased the size of this transition.

J. S. Kim, et al., Univ. Florida
Was this second transition ‘intrinsic’ to CePt$_3$Si or is it a second phase?

Do metallography first. What is metallography?

Metallographers examine polished cross sections of specimens from appropriate locations to determine the grain size, presence and distribution of second phase. Specimens are generally viewed in the as-polished condition first using brightfield illumination to observe those constituents that have a natural color reflectivity difference from the bulk of the metal. This procedure is commonly used to examine intermetallic compounds, . . . Can also use polarized light.
Metallography Picture of Grain Structure of Rhenium Metal
Result of Metallography of Ce-poor CePt3Si:

Lighter regions are second phase, with composition (determined by electron microprobe)

\[ \text{Ce : Pt : Si} \]

1 : 7 : 3.4 or

2 : 14 : \sim 7

J. S. Kim, et al.
And then the “a ha!” moment:
The Second Phase is not Ce$_2$Pt$_{14}$Si$_7$, it’s the well known, why didn’t I think of that, Ce$_2$Pt$_{15}$Si$_7$*

**Actually, the composition is Ce$_3$Pt$_{23}$Si$_{11}$**
Conclusion to the microprobe detective work

\( \text{Ce}_2\text{Pt}_{15}\text{Si}_7 \), according to further investigation by us, is an antiferromagnet at 0.4 K with a HUGE \( \Delta C/T \) of 22000 mJ/ Ce-moleK\(^2\) –

Certainly large enough to explain the second \( \Delta C_2 \) anomaly at 0.4 K in CePt\(_3\)Si that occurs with annealing (< 1% Ce loss)
Xray diffraction to probe structure and impurity phases: detective work II

The cubic A-15 structure materials (the high $T_c$ compounds before Bednorz and Muller, 1986) like $\text{Nb}_3\text{Sn}$ (used in magnets that have $H > 10$ T today) and $\text{Nb}_3\text{Ge}$ (previous record superconducting transition temperature $T_c = 22.8$ K) have a characteristic diffraction pattern of 3 lines, followed by 4 lines, followed by 3 lines.
FIG. 2. Diffraction trace of powdered Nb$_3$(Nb$_{0.82}$Ge$_{0.18}$). Note the lack of bcc Nb lines at 55.7 and 69.7 degrees 2θ.
Thermal Expansion of Pu Through Its Six Phase Changes

PRACTICAL CONSEQUENCES OF 5f ELECTRON BONDING

- $\alpha, \beta, \gamma$ phases are low symmetry crystal structures

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
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<tbody>
<tr>
<td>$\alpha$</td>
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<tr>
<td>$\beta$</td>
<td>B. C. MONOCLINIC</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>F. C. ORTHOROMBIC</td>
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<tr>
<td>$\delta$</td>
<td>F. C. CUBIC</td>
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<td>B. C. CUBIC</td>
</tr>
<tr>
<td>L</td>
<td>LIQUID</td>
</tr>
</tbody>
</table>

LENGTH CHANGE $\left( \frac{\Delta L}{L} \right)$

TEMP. °C
What happens to an X-ray pattern when a cubic system (e.g. fcc Austenite Fe-C steel) undergoes a tetragonal distortion (to bct Martensite)?
Lecture(s) on: The Unusual non-Fermi Liquid Behavior in Antiferromagnetic $U(Pt_{0.94}Pd_{0.06})_3$ – and all the sample prep. and characterization problems involved.
First, need to learn how to characterize materials via resistivity, magnetic susceptibility, and specific heat.
Resistivity, for example, is often used to detect superconductivity.

\[ \rho_{ab} = a + bT \]

2212

\[ a \approx 0 \]

\[ b \approx 0.4 \, \mu\Omega\, cm/K \]

123

\[ a \approx 0 \]

\[ b \approx 0.6 \, \mu\Omega\, cm/K \]
Resistivity measurements are conceptually quite easy.
But Beware!

- Contact resistance can play a large role (heating)
- When a sample is not homogeneous (< 3 d)
  e.g. TTF-TCNQ transition
And indeed, sometimes the geometry of the sample makes putting 4 spaced contacts easy.
Some ‘tricks of the trade’ for contacting samples

- Silver epoxy
- Silver ‘paint’
- Gold ‘paint’
- Spot welding (choice of wire, size)
- Forming a eutectic (e. g. Au-Ge)
Au ball bonding on doped Ge thermometers
Noise problems in resistivity measurements and their treatment

J. S. Kim, et al.
Measurement of Magnetic Susceptibility

- \( \chi = \frac{M}{H} \)

- In common use today, SQUID magnetometers from Quantum Design, Inc. can measure \( 10^{-4} \) emu easily (company quotes \( 1 \times 10^{-8} \) emu at 0.25 T), fields go typically to 7 T.
Measurement of Low Temperature Specific Heat I

Fig. 2. The silicon bolometer sample platform plus holder of the time-constant method calorimeter of Bachmann, Kirsch, and Geballe.
Measurement of Low Temperature Specific Heat II

MICRO CALORIMETER

G. R. Stewart
Why do we need **low** temperatures?

**Answer:** To determine the physics.

For example, when measuring the specific heat, $C$:

$$C/T = \gamma + \beta T^2 \quad / \quad \gamma \sim N(E_F),$$

the density of electron states at the Fermi energy.

$$\beta \sim 1/\Theta_D^3,$$

where $\Theta_D \sim$ lattice stiffness

If cannot cool the sample down to low enough temperature (typically $< \Theta_D/20$) so that a.) there is no $\delta T^4$ additional lattice term

b.) the electronic term $\gamma$ is not invisibly small vs the lattice $\beta T^2$ term.

then have trouble determining $\gamma$. 
SPECIFIC HEAT PARAMETERS $\gamma$ AND $\Theta_D$ FOR THE ELEMENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Symbol</th>
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<tr>
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<td>89</td>
<td>226</td>
<td>89</td>
<td>226</td>
<td>89</td>
</tr>
</tbody>
</table>

**Notes:**
- The table provides specific heat parameters $\gamma$ and $\Theta_D$ for the elements.
- Units of $m_J/g$-atom K$^2$.
- Notes, if any, are indicated by a value derived from elastic constant data.
Determining Physical Properties from Low T Specific Heat: the Debye temperature, $\Theta_D$, and the electronic density of states at the Fermi energy, $N(E_F)$

- Intercept of $C/T$ data with y-axis at $T=0$ gives $\gamma \sim N(E_F)$
- In the BCS theory of superconductivity, $T_c \sim \exp(-1/ N(E_F)*V)$
- Slope $= \Delta C/T \div \Delta T^2 = \beta$ 
  $\beta \sim 1/\Theta_D^3$
Noise Problems in the Measurement of C
Fig. 4. Two exponential decays, Eq. (14), under nearly identical conditions except that the lower curve is data in an 18-T normal state Bitter magnet, whereas the upper curve is in a 7-T superconducting, persistent mode magnet. Ge was used as a platform thermometer. A 20-s sweep is shown; the lower curve is the result of signal averaging eight sweeps to improve the signal-to-noise ratio.
Where does the noise in the lower tau curve come from?
Next, discuss: Preparation of UPt$_3$ alloyed with Pd via arc-melting
Preparation of UPt$_3$ alloyed with Pd via arc-melting
Melting Points, $T_m$, and Vapor Pressures at $T_m$ of U, Pt, Pd

- $T_{\text{melt}} = 1132, 1774, 1555 \, ^\circ\text{C (U, Pt, Pd)}$

- $T_{\text{vapor}} P = \leq 0.001 \, \text{mm, } \leq 0.001 \, \text{mm, } 0.01 \, \text{mm}$
Note that UPt$_3$ has a different structure (DO19 hexagonal) than that of UPd$_3$ (DO24 double hexagonal). The solubility of Pd in the DO19 structure is about $120\%$.

At the composition $U(Pt_{0.8}Pd_{0.2})_3$, the spin fluctuation term, $\sim T^3\log T$, is suppressed in the specific heat.
What happens at $U(Pt_{0.94}Pd_{0.06})_3$?

- It has been known since 1991 and Seaman, et al.’s discovery of the unusual properties of $U_{0.2}Y_{0.8}Pd_3$ that **non-Fermi liquid behavior** exists experimentally.
What is Fermi Liquid Behavior?

From a more theoretical point of view, a metal that is a ‘Fermi liquid’ at low temperatures is the same as the Fermi gas of weakly correlated electrons in the metal at room temperature, only – due to the strong correlations between the electrons at low temperatures – the low temperature ‘state’ of the electrons can be viewed as a collection of non-interacting ‘quasi-particles’ that have an increased effective mass, $m^*$. 
What is Fermi Liquid Behavior Experimentally?

- A metal that is a ‘Fermi liquid’ at low temperatures has the same physical properties as a Fermi gas:
  - both the specific heat/temperature $C/T$ and $\chi$ the magnetic susceptibility $\rightarrow$ constant at low $T$ while $\rho$ the electrical resistivity $\sim aT^2$
  - *but* with the constants increased $\propto m^*$
What is non-Fermi Liquid Behavior?

- Trivially, a metal that is a ‘non-Fermi liquid’ at low temperatures does not have $C/T$ and $\chi \rightarrow$ constant at low $T$.

Further, $\rho \sim a T^\alpha$, but $\alpha \neq 2$
Okay, now we know what properties non-Fermi Liquids don’t have. What properties \textit{do} they have?

- Often a ‘\textit{non-Fermi liquid}’ at low temperatures has $C/T$ and $\chi \sim \log T$ or $T^{-\alpha}$ (divergent). The resistivity is a little more varied, with $\rho \sim a T^\alpha$, $\alpha$ sometimes 1.0 or 1.5. However, almost always (stronger than ‘usually’), a \textit{non-Fermi liquid} does not occur \textit{below} a magnetic transition!
Where does nFl behavior occur?
At a Quantum Critical Point
A qualitative phase diagram for a quantum critical point for the case of three-dimensional antiferromagnetic interactions, after Millis (1993).
QCP Behavior where $T_N$ (2nd order) $\rightarrow 0$

Quantum Critical Point (quantum fluctuations dominate a large region (both in $\delta$ and to higher temperature) in the phase diagram.)
\( \text{U(Pt}_{0.94}\text{Pd}_{0.06})_3 \), however, has **non-Fermi liquid behavior** below \( T_{\text{Neel}} = 6 \text{ K} \)

- This fact has been known since 1992 (J. S. Kim, B. Andraka, and G. R. Stewart, “Possible Marginal Fermi Liquid Behavior in Doped UPt3,” Phys. Rev. **B45** 12081 (1992)) from measurements of the low temperature specific heat.
Magnetic Phase Diagram of $U(\text{Pt}_{1-x}\text{Pd}_x)_3$

Fig. 4.13. Phase diagram for the $U(\text{Pt}_{1-x}\text{Pd}_x)_3$ compounds for $x \leq 0.10$; Néel temperature, $T_N$, and superconducting transition temperature, $T_s$, vs. Pd concentration; $S =$ superconductivity, $SF =$ spin fluctuations, $AF =$ antiferromagnetism,
Low temperature C/T of $U(Pt_{0.94}Pd_{0.06})_3$

FIG. 1. Specific heat divided by temperature vs temperature of $U(Pt_{0.94}Pd_{0.06})_3$ from 0.3 to 9.5 K. Note the antiferromagnetic transition at $T_N = 6$ K. The solid line is a fit to the specific-heat data just below $T_N$ to serve as a background against which to compare the upturn in $C/T$ at lower temperatures.

J. S. Kim, et al.
Low temperature \((T < T_{\text{Neel}})\) \(C/T\) of \(U(\text{Pt}_{0.94}\text{Pd}_{0.06})_3\) shows \(C/T \sim \log T\)!

**FIG. 2.** Plotted here vs \(\ln T\) is the difference between the measured \(C/T\) for \(U(\text{Pt}_{0.94}\text{Pd}_{0.06})_3\) and the curve \((C = \gamma T + \beta T^3)\) shown in Fig. 1 fitted to the specific-heat data (five points) just below \(T_N\). As may be clearly seen, and as discussed in the text, this \(\Delta C/T\) follows a \((-\ln T)\)-temperature dependence between 0.3 and 4.3 K—independent of which fit is used for the background electronic, lattice, and spin-wave contributions.
Another look at the low temperature C/T of $U(\text{Pt}_{0.94}\text{Pd}_{0.06})_3$

A last look at the low temperature $C/T$ of $U(Pt_{0.94}Pd_{0.06})_3$
Distinguishing $\log T$ from $T^{-1+\lambda}$ (a digression for experts)

Low temperature data are important.

Graph from de Andrade, et al. PRL 81, 5620 (1998)
C/T \sim \log T \Rightarrow m^* \text{ diverges as } T \to 0

- What about the other measureable quantities like magnetic susceptibility, \( \chi \), and the electrical resistivity, \( \rho \)? Do they show non-Fermi liquid behavior?
Magnetic Susceptibility, $\chi$, of $U(Pt_{0.94}Pd_{0.06})_3$

$\chi$ (emu/mole) for $0.42 \, K < T < 5 \, K$ (X)

$U(Pt_{0.94}Pd_{0.06})_3$

$H = 0.5 \, T$

$U_{2}Zn_{17}$

$U(Pt_{0.94}Pd_{0.06})_3$
Magnetic Susceptibility, $\chi$, of $\text{U(Pt}_{0.94}\text{Pd}_{0.06})_3$ — initial results were not quite so problem free.
Magnetic Susceptibility, $\chi$, of $U(Pt_{0.94}Pd_{0.06})_3$

Implications/Meaning

- Note that $\chi \sim T^2$ as $T \to 0$, i.e. *Fermi liquid* behavior! What does this mean about the q-vector dependence of the magnetic fluctuations that cause the non-*Fermi liquid* behavior in the specific heat?
Electrical Resistivity, $\rho$, of $U(Pt_{0.94}Pd_{0.06})_3$
Electrical Resistivity, $\rho$, of $\text{U(Pt}_{0.94}\text{Pd}_{0.06})_3$

-initial sample’s results weren’t so good
Electrical Resistivity, $\rho$, of $U(Pt_{0.94}Pd_{0.06})_3$

- Initially, low T $\rho(H)$ data were noisy ($H=0$)
Electrical Resistivity, $\rho$, of $\text{U(Pt}_{0.94}\text{Pd}_{0.06})_3$

- Additionally, low T rho(H) data were very noisy (H = 18 T)
Electrical Resistivity, $\rho$, of $\text{U(Pt}_{0.94}\text{Pd}_{0.06})_3$

**Implications/Meaning**

- $\rho \sim T^2$, i.e. *Fermi liquid* behavior again, just like in $\chi$

- Therefore, in summary, even though the specific heat shows non-*Fermi liquid* behavior, both the magnetic susceptibility and the electrical resistivity show *Fermi liquid* behavior. This contradiction must mean (but this should be checked) that both $q=0$ (determines $\chi_{dc}$) and large $q$ (determines the dominant scattering processes in $\rho$) magnetic fluctuations in $\text{U(Pt}_{0.94}\text{Pd}_{0.06})_3$ are Fermi liquid in