EXAFS is a selective tool for investigating local atomic order around an atom, which is chosen to be the photoelectron emitter that tunes the energy of the photon to the binding energy of one of the core electrons. The photoelectron is a spherical wave. EXAFS is a low energy electron diffraction experiment of spherical symmetry in which the source of electrons is created inside the sample itself. Bond lengths, which intervene in the sine term (via the optical paths) for \( \chi(k) \), are clearly revealed in a Fourier transform of \( k\chi(k) \). Excellent determination is very often possible if phase shifts from a standard compound closely related in structure to the sample is available. Bond lengths in crystalline systems or molecules with high symmetry can be routinely determined with an accuracy of 0.01Å. Chemical identification of the neighbors requires a more sophisticated analysis. The energy dependence of both the amplitude and phase of the signal are specific to each element. Differentiation between two possible types of neighbors is easy if the atomic numbers differ by more than a few units. The backscattering amplitudes of two atoms (e.g. Al-Zn, Si-Ni, Ru-Fe, ...) can be in phase opposition over most of the full energy range. In such a case EXAFS is very sensitive to coordination numbers if these atoms are possible neighbors.

In most cases XAS data are collected in the classical transmission mode. The energy of the monochromatic beam is tuned by using double diffraction reflections from silicon crystals. Its intensity is measured before and after the absorbing sample with two different ion chambers. The values \( I_0 \) and \( I_1 \) are both recorded as a function of the photon energy, which is scanned step by step. \( \log(I_0/I_1) \) yields the cross section, \( \sigma(h\omega) \). For each point of the spectrum, a dead time allows for the mechanical movement and electronic stabilization. The time constant should be long enough to yield a noise reduced current in the typical range \( 10^{-12} \rightarrow 10^{-8} \) amps. In total each point needs about one second, half for dead time and half for photon counting. This procedure has a very high signal to noise ratio, since each measurement for \( I_0 \) and \( I_1 \) is made up of at least \( 10^9 \) photons.

An alternative scheme combines dispersive optics, which reflects a polychromatic X-ray beam and focuses it on the sample, with a cooled photodiode array, which is a position sensitive detector that can work under high flux conditions. A triangular shaped crystal is bent in order to cause a continuous change of the Bragg angle along the footprint of the beam on the crystal. The output for such X-ray optics is a polychromatic beam, but with correlation between the energy and the direction of propagation. This correlation transforms into an energy-
position correlation at the detector. After tuning the average incident angle to the Bragg angle for the energy of the edge, one can collect all the data at once, which takes advantage of the superior qualities of the silicon-based detector. The advantage of the dispersive mode over the step by step scan comes from the absence of mechanical movement and the simultaneous collection of the full data set, which gives extreme stability to the energy scale and hence high sensitivity to small changes in a series of closely related samples. This is typically the case for magnetic studies employing circular polarized X-rays to detect exchange splitting. In addition, the sample can be very small (<0.25 mm$^2$) which makes it feasible to do high pressure experiments with a diamond anvil cell. The fast and simultaneous acquisition opens the field to experiments in kinetics on the 100 ms to 1 s time-scale. This scheme, however, does eliminate the possibility for detection of the X-ray absorption signal via the intensity of the decay process and thus does not permit investigation of very dilute samples.

Detection of the decay process is an alternative way of measuring the creation probability of the photoelectron. The two main relaxation routes of the system to the fundamental state (Auger emission and fluorescence) are independent of the energy of the photon used to create the core hole. Thus the intensity of each decay process images only the energy dependent probability of creating the hole. Detection of relaxation processes are important for dilute systems such as a biophysical sample or an absorbate on a surface.

The fluorescence yield technique has been preferred generally for thick and dilute samples, since the absorption length of the fluorescent X-ray is a few μm. The use of an energy selective detector, the background is virtually eliminated. But such a detector generally covers a limited solid angle and so is inappropriate for collecting photons emitted over 4π. The game to play is to cover as large a solid angle as possible (a large fraction of 2π, since only a hemisphere is available). Due to the small mean free path of the electrons (between 5 to 500 Å according to their kinetic energy) electron yield detection is a surface sensitive method which has been generally regarded as possible only in ultra high vacuum. If the electron detector is tuned to the narrow energy window of the Auger electron, the SEXAFS (surface EXAFS) signal is coming from the upper part of the sample. If one wants to investigate deeper into the sample, one can include in the signal secondary electrons that are created by the Auger electrons after collisions due to the limited mean free path in matter. In the case of total electron yield the signal comes from the first 300Å or so. Often, partial electron yield is preferred since in most cases the investigator deals with a monolayer or less of absorbates on a surface of other materials. Here, there is no longer any ambiguity, as the signal comes from the true upper part of the sample since the
X-ray energy is tuned to the characteristic edge of the absorbate. REFLEXAFS combined with the fluorescence detection belongs to the same class of tools for studying thin two dimensional samples. Investigation of a buried interface is an example of the use of REFLEXAFS.

EXAFS is sensitive to clustering of matter. This property has been explored in many systems including catalysts, which is the reason for the interest displayed by major oil companies in X-ray absorption spectroscopy. The ability to detect surface segregation in small particles of binary alloys that are totally miscible in the bulk state and the findings of substrate induced shapes for these particles were the basic elements that initiated dozens of studies on catalysts.

The Al-Zn system is chosen here because it demonstrates the ability of EXAFS to distinguish between backscattering atoms since their respective phase shifts differ by roughly $\pi$. Chemical signatures provided by the complex backscattering factor is one of the key advantages of this structural technique over electron or X-ray scattering.

This phase shift related advantage appears erratically in neutron scattering, such as standard CuTi, where scattering lengths are of opposite signs, or when it is possible to use isotopes such as Ni to cancel the nuclear cross section. For neutron scattering this advantage is limited to dedicated systems. It is more widely encountered in EXAFS whenever elements belong roughly to the same column but differ by one row only.

Metastable Al-Zn solid solutions decompose into so-called Guinier-Preston zones spread within the depleted matrix when the initial concentration is within the miscibility gap. Hence Zn atoms are embedded in a Zn-enriched Al fcc lattice when the Al-6.8at%Zn solid solution is annealed for 50 days at room temperature.

The GP zone composition reaches 80% as determined by EXAFS. The first shell around Zn is then mostly made up of zinc atoms which yields the EXAFS spectra, displayed as fig.XV.15 in image 23 on the web site. The dotted line is the EXAFS spectrum of the stable Al-0.8at%Zn solid solution. In the latter case Zn atoms are surrounded by almost 12 Al atoms. The phase opposition between the two spectra is clearly revealed. It is related to the difference (close to $\pi$) between the two arguments of the complex backscattering amplitudes of aluminum and zinc (cf. fig.XV.14a in image 23). A progressive substitution, within the first shell around a central Zn atom, of aluminum neighbors by zinc neighbors should first decrease the amplitude of the EXAFS signal. Indeed a beat in $k$-space is observed. This is a point of zero amplitude that separates oscillations in the low $k$ domain, whose phase shifts are imposed by the aluminum atoms, from oscillations in the high $k$ range, dominated by the phase shifts of zinc. The beat node shifts from the higher to the lower energy range of the spectrum with increasing number of
zinc atoms inside the first shell as a result of clustering. Clustering trends appear because of the large initial concentration and/or the annealing of a metastable solution.

The first peak of the Fourier transform of the as-quenched metastable Al-4.4at%Zn solid solution is well reproduced by a mixture of 10.5 Al atoms with 1.5 Zn atoms in the first shell (fig.XV.16, curve 2 in image 23). Curve 3 (dotted line) shows a good fit to the Fourier transform of the as-quenched metastable Al-6.8at%Zn solid solution. Curve 4 (crosses) exhibits the surprising split peak, which is the theoretical Fourier transform of an EXAFS simulated spectrum mixing 7 Al atoms and 5 Zn atoms in the first shell. This was experimentally observed when clustering is advanced (the metastable Al-4.4at%Zn solid solution annealed at room temperature for 12 days or the metastable Al-6.8%Zn annealed at room temperature for 90 minutes). More generally, all the supersaturated alloys investigated, with compositional ranges from 4.4at% to 15at%, decompose via a common sequence of EXAFS spectra, but with different time scales.

In this particular case where the system is well conditioned to yield a significant signal, namely a heavy atom in a light matrix plus a difference of π in the phase shift, EXAFS is able to determine the coordination number with an accuracy of 0.25 atom. In addition the first shell radii are routinely measured with a precision of 0.01Å.

Covalent pseudobinary alloys (Ga$_x$In$_{1-x}$As) with the zincblende structure have been investigated by EXAFS to test the virtual crystal approximation against the contradictory notion of invariant covalent radii introduced by Linus Pauling. A virtual crystal model gives a stacking of atoms in an average position of the zincblende structure. It is found by means of X-ray diffraction that the off-site position of the atoms is distributed at random. In the real crystal the position of the As atom is no longer at the center of a tetrahedron if the coordination is heterogenous. The first demonstration of departure from the virtual crystal came from EXAFS.

For determination of the anion-cation (b* distance), anion-anion, cation-cation, three spectra are available in addition to Bragg diffraction, which gives the average lattice parameter with respect to x. A similar study has been extended to ioniically bonded compounds (K$_x$Rb$_{1-x}$Br and RbBr$_x$I$_{1-x}$) with the rocksalt structure. For clarity only the results for the covalent alloy are presented, but similar conclusions are drawn when the substitution takes place within the anion sublattice.

The first neighbor distribution around one or the other cation is rather simple. It does not differ from a pure binary system. It consists of 4 As neighbors at a well defined distance close to that of the pure binary compound GaAs or InAs,
according to the cation that is probed. But a small composition dependent differ-
ence exists. Arsenic is at the center of five possible tetrahedra according to the
number of Ga (or In) at the apex of this geometrical unit with a defined Ga-As
and In-As distances. It is assumed that the cations sit exactly on the sites of the
fcc sublattice of the zincblende structure, whereas As is off-center in intermediate
tetrahedra where one of the cations differs from the others. (See fig.XV.17 in
image 23 on the 09-801 web site.)

The second neighbor distribution is more complex. Close anions are bonded
via a cation which can be one or the other. The anion-anion distribution is
bimodal with As-Ga-As and As-In-As distances close to those in pure GaAs and
InAs, respectively. The cation-cation distribution consists of a single broadened
peak at the virtual crystal distance.

For Zn(Se$_{x}$Te$_{1-x}$) which is more ionic and has anion substitution rather than
cation substitution, the situation is almost identical. For the rocksalt type ionic
compounds the results follow a similar scheme but is a little more complicated
since there are six neighbors in the first shell instead of four.

The main difference between covalent and ionic alloys is that the composition
dependence of the cation-anion distance is larger for the ionic case. This difference
may be reasonably explained by considering compressibility. It cancels in similar
metallic solutions.

Analysis of XANES spectra is a many body problem that requires a conﬁgura-
tion interaction of at least two states. This is a region of low energy electrons
(< 30 eV) where valence states of the sample come in to play. The symmetry
of the photoelectron itself in the core hole relaxation process is important in the
XANES region where transitions to antibonding or non bonding orbitals can be
found. The first excitation in cuprates, for example, is a charge transfer from
the ligand to the transition metal (d$^9$−d$^{10}$L$^-$), where L$^-$ represents a hole in the
anion valence band. The ground state of the square planar cuprates may be well
described by the admixture of conﬁgurations

$$\alpha_0 |3d^9 > + \beta_0 |3d^{10}L^- >$$

and for a nickelate (NiO$^{6-}$) the admixture is

$$\alpha_0 |3d^8 > + \beta_0 |3d^9L^- >$$

with

$$\alpha_0^2 + \beta_0^2 = 1.$$

For the final state one must take into account the presence of the core hole and
let the system relax in order to screen the perturbation. The gain in Coulomb
energy, due to the interaction between the core hole and the quasi-localized d-electrons puts the $3d^n$ ($n < 10$) poorly screened configuration at higher energy than the $3d^{n+1}L$ well screened one and changes their admixture. In the final state, the configurations $|f_1>$ and $|f_2>$:

$$
|f_1> = +\alpha_f|\xi\ldots3d^n\ldots e_k> +\beta_f|\xi\ldots3d^{n+1}L\ldots e_k>
$$

$$
|f_2> = -\beta_f|\xi\ldots3d^n\ldots e_k> +\alpha_f|\xi\ldots3d^{n+1}L\ldots e_k>
$$

and

$$
\alpha_f^2 + \beta_f^2 = 1.
$$

e_k represents the photoelectron with a wave vector $k$. $\xi$ is a core hole (1s half empty). $|f_1>$ is at lower energy than $|f_2>$ and has dominant $3d^{n+1}L$ character ($\beta_f^2 > \alpha_f^2$). This two-configuration concept accounts for the Cu K-edge XAS spectra of divalent compounds with O or N ligands, which exhibit systematic double features, split by a nearly constant value of 7 eV, always found in divalent copper compounds. The role of the slow photoelectron in XANES appears qualitatively in the anisotropy of the relaxation process. We account for this for our admixture of configurations by specifying the momentum of the photoelectron as perpendicular ($k_\perp$) or parallel ($k_\parallel$) to the square planar unit, according to the direction of polarization of the incident photon. $k_\perp$ and $k_\parallel$ lead to ($\alpha_f^\perp$ and $\beta_f^\perp$) and ($\alpha_f^\parallel$ and $\beta_f^\parallel$), respectively.

The charge transfer process in the relaxation of the core hole state is a filling of a d hole. For the electron transfer O2p $\rightarrow$ Cu3d in cuprates only one channel ($x^2 - y^2$ in plane symmetry) is available. But with nicklates two equivalent channels ($x^2 - y^2$ in plane and $3z^2 - r^2$ out of plane) are opened with equal probability. Depending on the symmetry of the photoelectron, which can be excited in plane ($x,y$ symmetry) or out of plane ($z$ symmetry), one expects a different behavior in the final states for cuprates and nicklates.

Two sets of angle resolved Cu K-edge and Ni K-edge XAS experiments on single crystals of La$_2$CuO$_4$ and Pr$_2$NiO$_4$ show that the admixture of configurations in the final state is anisotropic for cuprates ($\alpha_f^\perp \neq \alpha_f^\parallel$) and ($\beta_f^\perp \neq \beta_f^\parallel$) but shows no anisotropy for nicklates.

This anisotropy is specific to the square planar geometry of Cu(II), since it is a property due to the existence of a unique non-degenerate channel available for the O2p $\rightarrow$ Cu3d transfer. Obviously, this anisotropy should not exist in analogous nicklates. When one channel of the relaxation is attenuated by the photoelectron $e_k^\parallel$ or $e_k^\perp$, the other one is free to get the oxygen $2p_x$ or $2p_{x,y}$ electron transferred. The experimental results are shown in figures XV.17 and XV.18 in image 23 on our web site. They should be relabelled XV.18 and XV.19