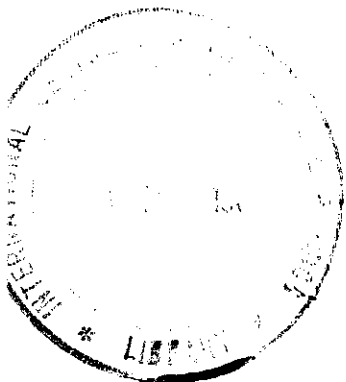




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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

NEUTRON AND X-RAY SCATTERING FROM
METALLIC ALLOYS, EXAFS

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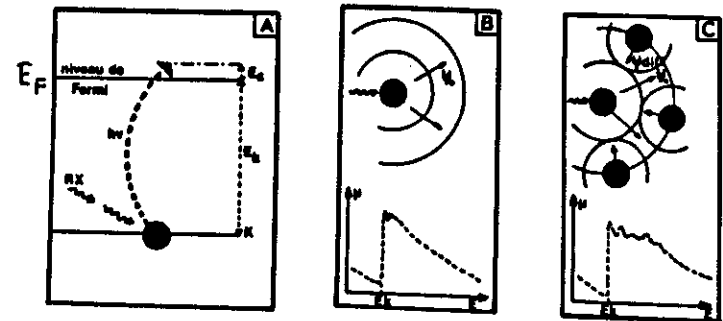
PART IV : EXAFS

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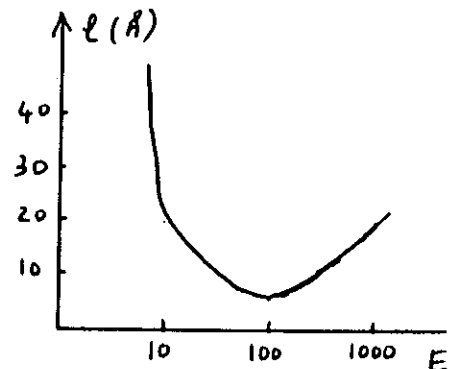
IV EXAFS

IV.1. Introduction

In a molecule, a liquid or a solid, one observes oscillation of the X-ray absorption coefficient μ up to ≈ 1000 eV above the edge. These features, which are not found in free atoms or gases, are attributed to the presence of near neighbours, and designed by the name EXAFS ("Extended X-ray fine structure").

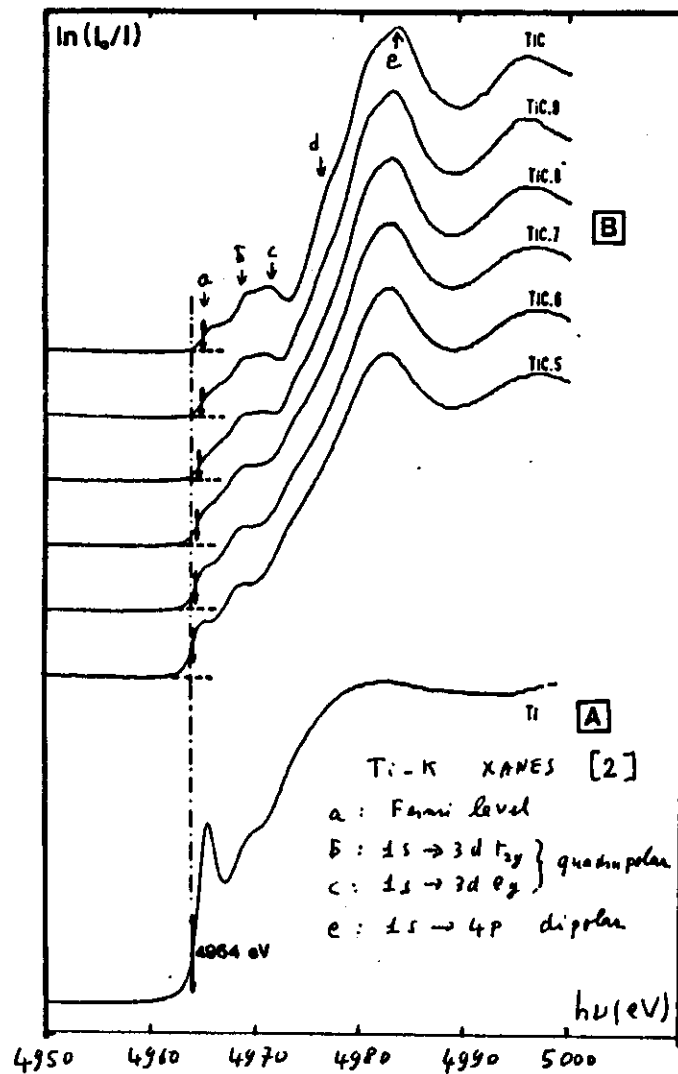


In the present interpretation of X-ray absorption coefficient structures, one distinguishes two regions, mainly because of different values of the photoelectron mean free path ℓ :



- For a kinetic energy $\lesssim 20$ eV, ℓ is large (> 10 Å), and the photoelectron, propagating in large regions of the solid, is sensitive to the band structure; in this region, $\mu(E)$ is called XANES (X-ray absorption near edge structure), and its shape is in first approximation related

to the partial local density of states of the core quantum number (i.e. p local density of states for a K absorption edge, corresponding to creation of a hole in the $1s$ core shell, with the dipolar selection rule $\Delta l = \pm 1$); in a metal, where the hole created by the ejected photoelectron is immediately screened by the conduction electron gas, $\mu(E)$ in the XANES region gives information on the unoccupied partial density of states [1], and also in compounds, on the charge transfer (see figure).



- For a kinetic energy > 50 eV (EXAFS region), l is of the order of 5 to 10 Å, and the photoelectron sees only the near neighbour shells of the emitting atom; in fact, the oscillations of μ are explained by an interference between the outgoing photoelectron wave and the wave backscattered by the neighbours. Therefore, these EXAFS oscillations will appear as a local probe of the atomic structure. It informs on near neighbour distances, coordination numbers, mean square random displacements (thermal vibration amplitudes, ...) around an atom of specific chemical nature.

For review articles, the reader should see references [3] and [4].

IV.2 The basic EXAFS formula

The EXAFS function in a solid is defined as

$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$, where $\mu(E)$ is the measured absorption coefficient and $\mu_0(E)$ the non oscillating atomic value.

In first approximation, $\mu(E)$ is given by the dipolar approximation and Fermi golden rule: $\mu(E) \propto |\langle i | e \vec{E} \cdot \vec{r} | f \rangle|^2 N(E_f)$, $\vec{E}$ electric field of the radiation, $|i\rangle$ initial state (i.e. $1s$ core), $|f\rangle$ final state, $N(E_f)$ density of states at the final state energy.

Above 30 eV of the Fermi level E_F , the photoelectron has a large kinetic energy and can be approximated to a free electron, with energy $E_f = E - E_0 = \hbar^2 k^2 / 2m_e$ (k : photoelectron wave vector, E_0 threshold energy not very different from E_F).

For establishing the basic EXAFS formula for a K -edge, the following approximations are made (and at least partly justified):

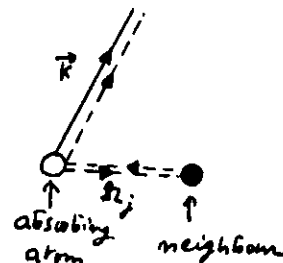
- Weak scattering (Born approximation, 1st order perturbation), superposition of scattered amplitudes, neglect multiple scattering, interference only between:

- the outgoing wave (—)
- the electron wave outgoing the central atom, backscattered by the neighbour and rescattered by the central atom,

(the phase shift between the 2 waves

is $2\lambda_j + \psi_j(k)$, with $\psi_j(k) = \varphi_j(k, \pi) + 2\delta_j^2(k)$

↑ neighbour phase shift ↑ central phase shift



- the electrons which have suffered inelastic scattering due to their mean free path l do not participate to the interference, whence a $e^{-2\lambda/l}$ damping term;

- the neighbour atoms are distributed into shells around the central atom, defined by the distance λ_j , and a spherical average is made;

- thermal vibrations introduce for each shell a damping factor (because photoemission is instantaneous, one must make an average on all positions); this will be the case also for static distortions; if the displacements are small, their effect is simulated by a Debye-Waller type factor $\exp(-2\sigma_j^2 k^2)$, where σ_j^2 is the mean-square relative displacement between atoms on shell j and central atom;

$$- \kappa \lambda_j \gg 1$$

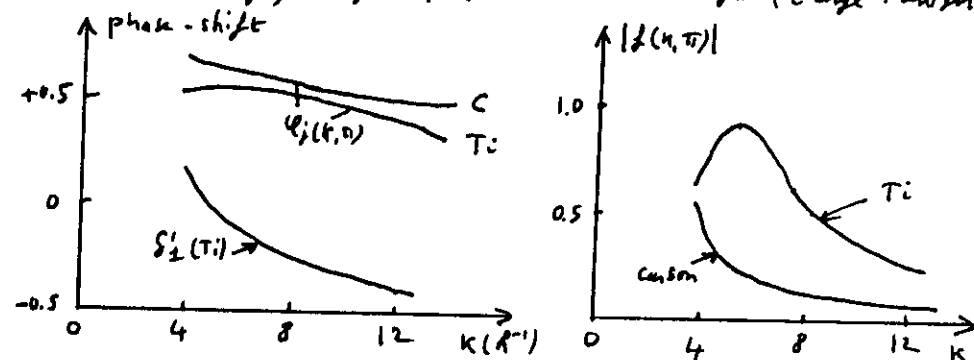
The EXAFS master formula for a K-edge may then be written:

$$\chi(k) = \sum_j \chi_j(k) = - \sum_j \frac{N_j}{k \lambda_j^2} |f_j(k, \pi)| \sin(2\kappa \lambda_j + \psi_j(k)) e^{-2\sigma_j^2 k^2} e^{-\lambda_j/l(k)}$$

Each neighbour shell j participates to the EXAFS by a damped oscillatory function, proportional to the N_j number of atoms in the j -th shell, and to $|f_j(k, \pi)|$ the backscattering amplitude

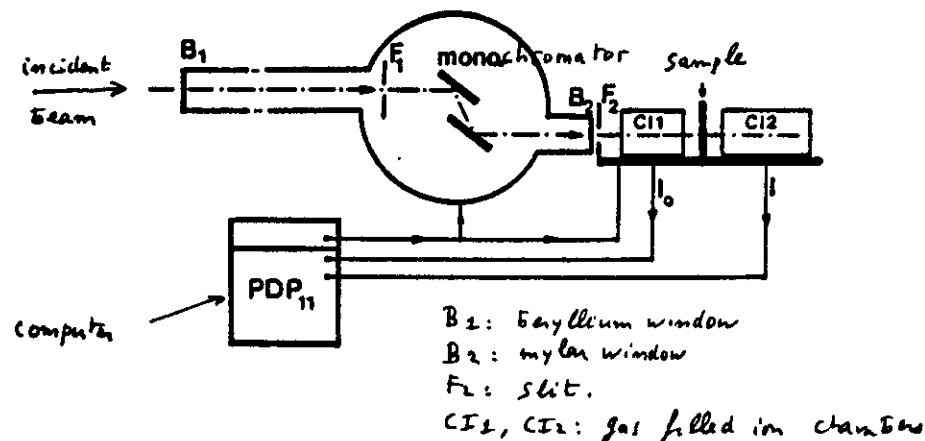
of these atoms.

$|f_j(k, \pi)|$ and the phase shifts $\varphi_j(k, \pi)$ and $\delta_j^2(k)$ have been theoretically calculated for neutral atoms by TEV and LEE [5]: an example is shown below. Of course, in materials with partial ionic bonding, they depend on the local charge (charge transfer,



IV. 3 Experimental aspects

A typical EXAFS apparatus is schematized below.



Experiments are generally made by transmission. The thickness of the sample has to be optimized (generally a few μm); single crystals are not necessary.

One has to use a continuously tunable X-ray source, i.e.

- Synchrotron radiation,
- or the white beam (Bremsstrahlung) of a conventional X-ray source (to have a large intensity, take a rotating anode system).

(6)

The resolution in energy must be better than 5 eV; the monochromator can be channel-cut silicon (for synchrotron radiation, the change of wavelength requires only vertical displacement of the sample), or focusing monochromator for less intense conventional X-ray sources.

Typically, with the EXAFS spectrometer 1 of LURE (JCT, Orsay, France), for the Ti-K absorption spectrum, the experiment is made for incident energy between 4 and 6.5 keV, i.e. $1.9 < \lambda < 3.1 \text{ \AA}$, with an energy resolution of $\approx 1.2 \text{ eV}$ at 5 keV; the duration of an experiment is typically 1 hour.

For structural determinations, a cryostat (helium gas, 10 K, mylar windows) allows to diminish the damping due to thermal vibrations.

Usual X-ray sources allow to study easily the EXAFS spectra corresponding to the K-edge of transition elements (first row) and to the L-edges of heavier elements (rare earths).

EXAFS on light atoms such as Al requires soft X-rays (K edge of Al: 1559 eV, i.e. $\lambda \approx 8 \text{ \AA}$).

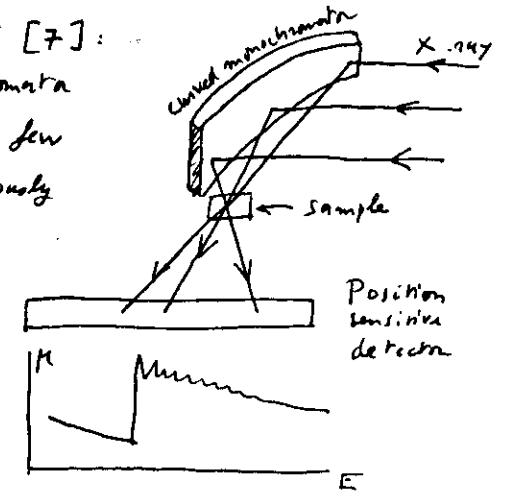
Other techniques

- Measurements of the products of absorption: fluorescent radiation, or Auger or secondary electrons (in reflexion geometry); because the measured intensity is proportional to the number of holes created by the X-rays, it is proportional to the absorption coefficient of the considered atom. These techniques are in particular used for small concentration of absorbing centers: their sensitivity depends on the relative atomic

number of matrix and element; fluorescence is generally preferred to transmission for detection lower than typically 10^{-2} to 10^{-3} , especially for low Z atoms in high Z matrix. Auger or secondary electrons allow surface or thin film studies (SEXAFS), down to a fraction of monolayer adsorbate (iodine on copper [6]).

- Dispersive mode EXAFS [7]:

the use of a curved monochromator gives a range of energies (a few 10^2 eV); recording simultaneously the EXAFS spectrum on a position sensitive detector, allows kinetic experiments at the scale of 10^{-2} s .



(7)

IV. 4. Treatment of data

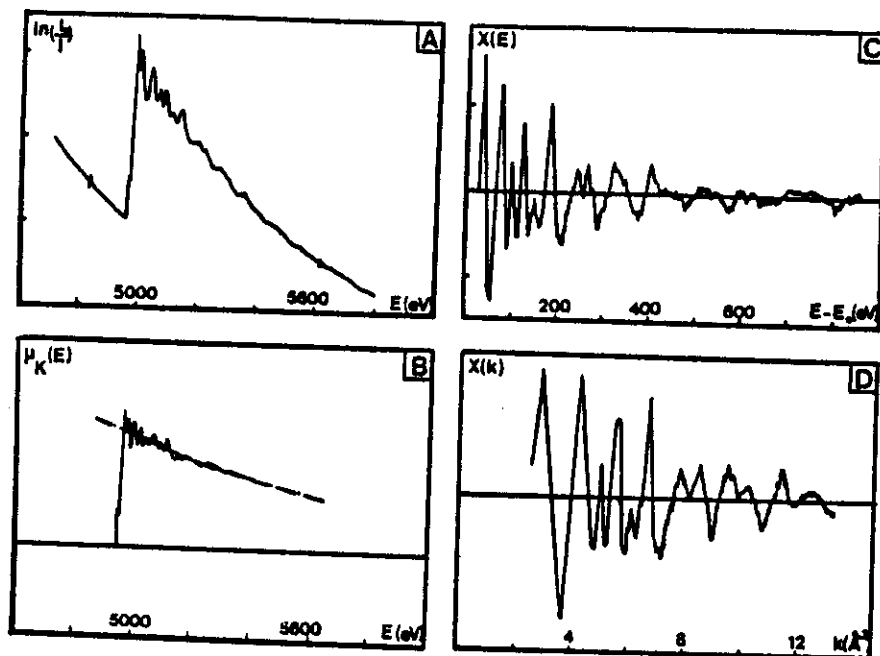
A: Measurement of the experimental spectrum $\mu = \ln(I_0/I)$

B: Isolate the contribution of K-edge

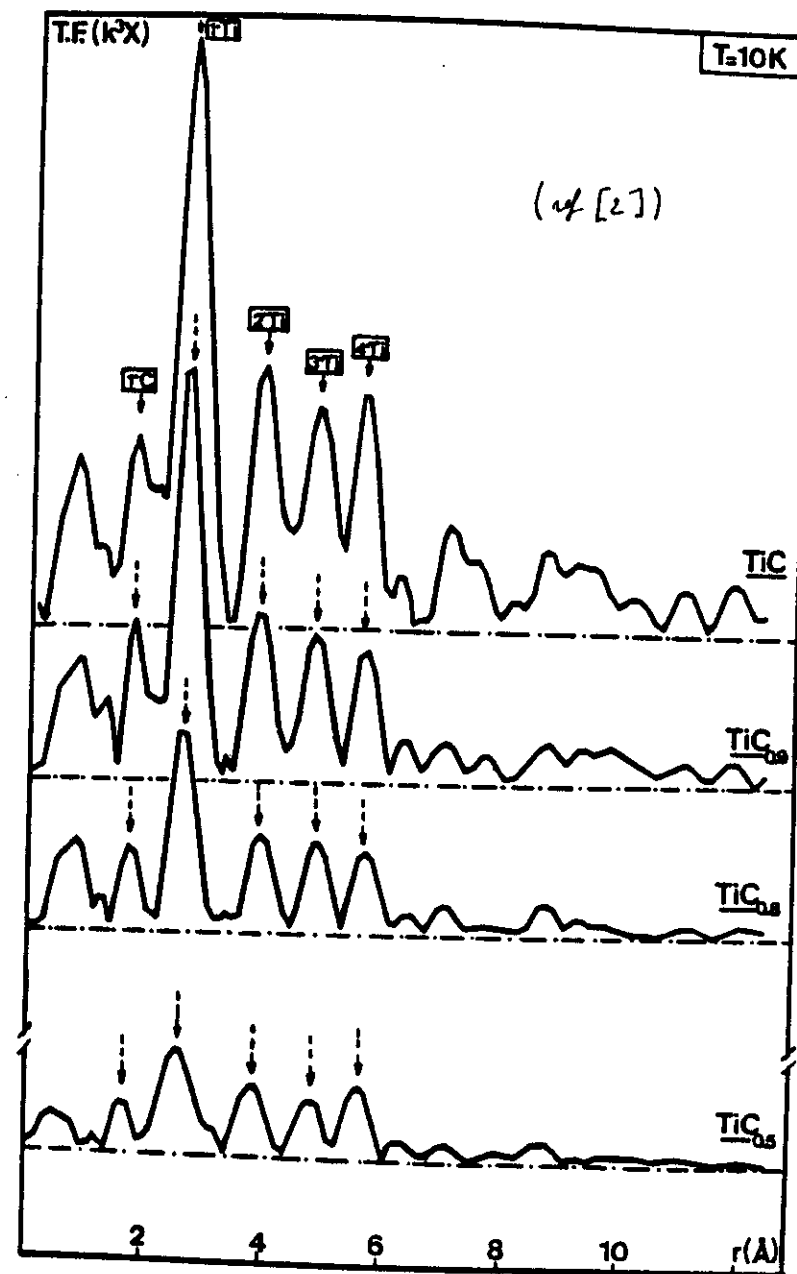
C: Obtain normalized $\chi(E)$ using a polynomial modelling of $\mu_0(E)$

D: Obtain $\chi(k)$ with $k = \sqrt{2m(E-E_0)}/\hbar$, with the delicate choice of E_0 (which is near E_p within a few eV): generally E_0 is taken as an adjustable parameter to optimize the k-independency of calculated interatomic distance $R_i(k)$.

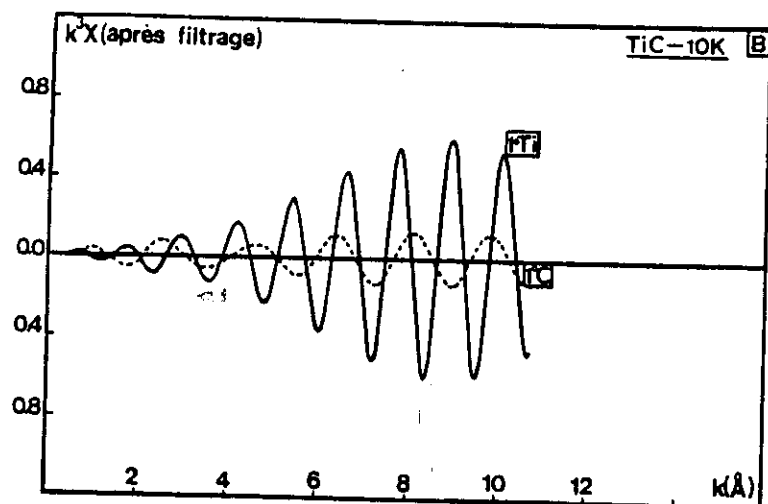
(see figure next page, from ref. [2]).



To obtain the individual $\chi_i(k)$ for each shell, one makes a Fourier transform, generally of $k^3 \chi(k)$ to amplify the weight of the high energy oscillations: typical Fourier transforms are shown on next figure. Each peak corresponds to a neighbours shell of the absorbing atom; it can be individually separated, and an inverse Fourier transform gives $\chi_i(k)$ for each shell. Care has to be taken with the Fourier transform window, which in the case of Ti-K EXAFS is taken between $k_{min} = 2 \text{ \AA}^{-1}$ (below which the EXAFS approximation is no more valid) and $k_{max} = 12 \text{ \AA}^{-1}$ (above which the ^{damped} EXAFS oscillations disappear in the background).



Fourier transform of the K-Ti EXAFS spectra of NaCl type structure TiC_{1-x} , measured at 10 K. Damping due to static relaxations ($\approx 0.1 \text{ \AA}$) around carbon vacancies.



Fourier transform filtered partial EXAFS $k^3 X_j(k)$ for Ti and C first neighbours of a Ti absorbing atom in TiC (10 K) (cf [2])

The nodes of $X_j(k)$ give the annihilation points of $\sin(2k\lambda_j + \psi_j(k))$:

- if the phase-shift $\psi_j(k)$ is known, one obtains the distances of neighbour shells, λ_j ;
- if λ_j is known (pure metal or compound of known crystal structure), $\psi_j(k)$ measured can be compared to the theoretical values,
- generally one has a reference compound A of known λ_j , allowing to determine experimentally $\psi_j(k)$; then one assumes on the basis of similar electronic structure a transferability of phase shifts and deduces λ_j for the unknown compound B (for example A = crystal, B = amorphous).

The amplitude ratio of the partial EXAFS $X_j(k)$

for compounds A and B gives information on the change of coordination number for the j -th shell, and on Debye-Waller factors, assuming unchanged mean free path $\ell(k)$:

$$\ln \left[\frac{X_j^A(k)}{X_j^B(k)} \right] = \ln \left[\frac{N_{jA}}{N_{jB}} \frac{\lambda_{jB}^2}{\lambda_{jA}^2} \right] + 2(\sigma_{jB}^2 - \sigma_{jA}^2) k^2$$

(plot $\ln(X_j^A/X_j^B)$ versus k^2)

IV. 5 Applications

(a) Dilute aluminium alloy

RAOUX et al [8] measured the K EXAFS spectra of the solute in Al - 2% Cu, Al - 0.8% Zn and Al - 3% Mg, solid solutions (with no clustering). They found respective variations of -0.125, -0.02, +0.08 (± 0.05) Å of the first neighbour solute distance compared to pure Al. This allowed to show that the elastic theory of continuous medium, as well as the lattice static theory failed to give the correct magnitude of the local relaxation (factor 2 at least).

After aging, the formation of Guinier-Preston zones was followed in Al-Cu 2%. By the previous group [9] and LENGELER and EISENBERGER [10] who obtained similar results. The fit of the data showed that G.P. zones are monolayers of 50% Al-50% Cu composition. Within the zone, the Cu-Al and Cu-Cu distances are equal to that in the pure Al matrix, i.e. 2.86 Å. The contraction between the zone plane and the neighbouring (100) Al plane is found to be $17 \pm 2\%$ [9].

(b) Irradiated Al-Zn [11]

$2 \cdot 10^{-4}$ Frankel pairs were created by 2.5 MeV electron irradiation of dilute Al-Zn (1000 ppm Zn). The k-Zn EXAFS was measured on the sample as-irradiated and subsequently annealed from 80 K. The specimen annealed

at 300 K, where complete recovery occurred, was taken as reference, and the weighted difference gave the EXAFS of the Zn atoms ($\approx 15\%$) which had trapped an interstitial. The analysis of the results showed that most of the Zn atoms sit in interstitial octahedral sites, whereas the Al interstitial occupies the same Zn site. (12)

(c) Internal oxidation of Cu-Fe [12].

A dilute Cu alloy containing 75 ppm Fe was oxidized in air (10^{-4} Torr) then at 1000°C , and the EXAFS measured by Fe-K X-ray fluorescence, with a focusing crystal analyzer to improve the signal-to-noise ratio. In the reduced alloy, Fe was found dilute (no Fe-Fe pairs). But in the oxidized alloy, the EXAFS showed clustering of the Fe atoms, altogether with Fe-O and Fe-Cu pairs, but the local order does not correspond to CuFe_2O_4 .

(d) Topologically disordered systems and limitations of the basic EXAFS formula

The insufficiency of the classical EXAFS formula of § II.2 appeared first from a study of pure Zn, where this analysis predicted a contraction of $0.09 \text{ \AA}$ from 20 to 300 K, compared to the known thermal expansion of $0.05 \text{ \AA}$; there was also an apparent decrease of coordination number. Similar observations arose from the study of the Ti-Ti first neighbor distance and coordination in TiC when introducing carbon vacancies (up to 50%) [2]. EISENBERGER and BROWN [13] proposed a generalized formalism allowing to treat a non gaussian or broad distribution of interatomic distances. In particular, an asymmetric distance

distribution, due to anharmonic effects, was shown to lead to an apparent contraction and loss of neighbors.

Criteria are given by [13] for the application of the classical formula:

$$\frac{\langle u_j^2 \rangle}{r_j^2} < 0.01 \text{ \AA}^2, \quad k^3 \langle u_j^2 \rangle \ll 1$$

(u_j : fluctuation of distance of the j -th neighbor shell).

For the study of amorphous systems, model functions have to be taken for the pair distribution function [4]. For the Ti-C system, an improved formula, taking into account the asymmetric Ti-Ti distribution distance, showed that each vacancy repelled its Ti first neighbor by $0.08 \text{ \AA}$; a model with superposition of the displacement fields of the vacancies is satisfactory at least up to 30% vacancies [2].

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