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# **XAFS** applications in semiconductors

WEI Shi-Qiang<sup>1\*</sup> SUN Zhi-Hu<sup>1</sup> PAN Zhi-Yun<sup>1</sup> ZHANG Xin-Yi<sup>2</sup> YAN Wen-Sheng<sup>1</sup> ZHONG Wen-Jie<sup>1</sup>

(<sup>1</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China; <sup>2</sup>Department of Physics, Surface Physics Laboratory (National Key Laboratory), and Synchrotron Radiation Research Center, Fudan University, Shanghai 200433, China)

**Abstract** X-ray absorption fine structure (XAFS) has experienced a rapid development in the last three decades and has proven to be a powerful structural characterization technique nowadays. In this review, the XAFS basic principles including the theory, the data analysis, and the experiments have been introduced in detail. To show its strength as a local structure probe, the XAFS applications in semiconductors are summarized comprehensively, that is, thin films, quantum wells and dots, dilute magnetic semiconductors, and so on. In addition, certain new XAFS-related techniques, such as in-situ XAFS, micro-XAFS, and time-resolved XAFS are also shown.

**Key words** X-ray absorption fine structure (XAFS), Local structures, Semiconductor quantum system, Synchrotron radiation

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## 1 Introduction

X-ray absorption fine structure (XAFS) has been recognized as a powerful structural characterization method, whose most striking advantages are its element-specificity, sensitivity to the short-range order (typically several Å) and chemical state. XAFS can provide quantitative structural information at an atomic scale around the specific atom, that is, near-neighbor species and distance, coordination number, and fluctuation in bond distance. The distance determination can be accurate to about 0.01 Å or better. The sensitivity to the short-range order makes XAFS capable of probing the local structure for a diversity of systems, no matter whether the studied sample is in a solid (crystalline or amorphous), liquid, or gas state. Using high-brilliance synchrotron radiation (SR) light sources, many kinds of measurement methods have been developed to obtain high-quality XAFS data, such as transmission XAFS for usual material, fluorescence XAFS for dilute impurity, and thin film, magnetic XAFS for spin study, *in situ* (high-temperature, high-pressure) XAFS for state or stress transformation investigation, grazing-incidence XAFS for surface research, space-resolved XAFS and even time-resolved XAFS for dynamics. Nowadays, XAFS is routinely used in a wide range of scientific fields, including physics, chemistry, biology, materials sciences, environmental sciences, and so on. In this review, the focus is mainly on the semiconductors.

#### 1.1 Definition of XAFS

XAFS describes the details of how X-rays are absorbed by materials at energies near and above the absorption edge of a selected atom. It refers to the oscillatory structure in the X-ray absorption coefficient  $\mu(E)$  just above the absorption edge. As an example, Fig. 1 shows the Ge *K*-edge XAFS spectrum of mono-

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<sup>\*</sup>Correspondent author, E-mail: sqwei@ustc.edu.cn

crystalline Ge powder. Generally, XAFS is divided into two regimes: extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). EXAFS refers to the oscillations observed over a wide energy range extending for 1000 eV or more above the edge, while XANES denotes the fine structures around an absorption edge extending typically 30 ~ 50 eV. The fundamental physics of EXAFS is similar to that of XANES. The only distinction of them is the complexity of their spectra.



Fig.1 Ge K-edge XAFS spectrum for monocrystalline Ge powder.

Due to the nature of the absorption process, XAFS spectra are sensitive to the electronic structure and local atomic structure of the selected atom <sup>[1]</sup>. In particular, XANES can distinguish the electronic state and local coordination geometry (including atomic types, bond angles, and distances) surrounding a specific atom. EXAFS is sensitive to the distance, coordination number, and species of the atoms immediately surrounding the selected element. As a powerful structural probe, XAFS has provided a relatively simple and practical way to determine the chemical state and local atomic structure in a variety of systems.

#### 1.2 History of XAFS

The XAFS phenomenon was first observed by Friche and Hertz in 1920<sup>[2]</sup>. However, the understanding of this phenomenon has long been controversial. In 1931, Kronig originally interpreted the XAFS oscillations in crystals as a density-of-states effect in terms of the so-called long-range order (LRO) theory <sup>[3]</sup>. But attempts to match EXAFS peaks with predictions of LRO theories proved unsatisfactory, and afterward in 1932, Kronig presented an alternative theory for small molecules <sup>[4]</sup>, where the oscillatory structure in EXAFS was attributed to the influence of the neighboring atoms on the transition matrix element in the golden rule, that is, a short-range order (SRO) effect. The debate between the LRO and SRO theories remained for 40 years until in 1971 the pioneering study by Sayers, Stern, and Lytle performed the k-space Fourier transform to separate peaks corresponding to various atomic shells <sup>[5]</sup>. After that it is widely recognized that the SRO theory is more appropriate in interpreting the origin of XAFS. Another key development in the XAFS theory is that of an accurate treatment of multiple-scattering (MS) effects. In 1975, Lee and Pendry first proposed the theoretical treatment of multiple-scattering EXAFS in terms of effective path length <sup>[6]</sup>. This approach takes the advantage of the Fourier transform in the EXAFS data analysis. A major advance in the path-by-path XAFS theory, which overcomes all the major computational difficulties, is based on a separable representation of the Green's-function propagators developed by Rehr and Albers <sup>[7, 8]</sup>. With the use of the second-generation machine, XAFS theory was improved gradually <sup>[9, 10,</sup> <sup>11, 12]</sup> adapted to better resolved fine structures in the experimental spectra. Nowadays, nearly all parameters (e.g. temperature <sup>[13]</sup>, angular <sup>[14, 7, 15]</sup>, and spin <sup>[16]</sup> dependence) are fixed by ab initio starting conditions, except the treatment of multi-electron excitations (MEEs) which is phenomenologically described by an amplitude reduction factor  $S_0^2$  (Eq. (1) in the following section) weakly depending on energy only and approximated by a constant in practical calculations <sup>[17]</sup>. So far, various advancements in the theoretical models have been obtained, such as full multiple-scattering (FMS)<sup>[18]</sup>, self-consistent field, and fully relativistic calculations [19] especially for a quantitative analysis of the near-edge regime. Different approaches also address the interaction of the core hole with the photoelectron and thereby pave the way for the theoretical description of an excited state spectroscopy <sup>[19,</sup> <sup>20]</sup>. Recently, theoretical standards eliminated the arbitrariness in the experimental analysis as it was done in the early days by means of tabulated standards <sup>[21]</sup>. The EXAFS theory is implemented in various ab initio codes, such as CONTINUUM <sup>[22]</sup>, EXCURV <sup>[23]</sup>, FEFF <sup>[19]</sup>, GNXAS <sup>[24]</sup>, WIEN2k <sup>[25]</sup>, the Munich

SPRKKR package <sup>[26]</sup>, NSRL- XAFS <sup>[27]</sup>, and others <sup>[12]</sup>.

It should be remarked that the controversy between the early XAFS theory, that is, SRO and LRO, actually lies in the energy-dependent competition between scattering strength and inelastic losses. The excited high-energy photoelectron state is not infinitely long lasting, but decays as a function of time and distance and hence cannot probe long-range effects. This decay is due to the inelastic losses (extrinsic losses) as it traverses the material, and the intrinsic lifetime of the core-hole state (intrinsic losses). Therefore, the excited photoelectron outgoing wave dies away as it moves further away from the absorbing atom and becomes too weak to significantly reflect any waves off of distant atoms. The net effect is that XAFS can only measure the local atomic structure within a range limited by the effective mean free path of the excited photoelectron. This range is typically on the order of tens of angstroms.

Furthermore, it turns out that a fully quantitative treatment of the near-edge structures is still challenging. This is due to various many-body effects, such as the photoelectron-core hole interaction, multiplet effects, the photoelectron self-energy and inelastic losses. Various theoretical treatments are based on the final state rule in a one-electron approach. A different approach for the calculation of the near-edge structures is the atomic multiplet theory <sup>[28]</sup>. Unfortunately, both approaches have their specific drawbacks <sup>[29]</sup>. Recently, in certain works, a GW approach was used <sup>[30]</sup>. Another approach is based on a time-dependent density-functional theory (TDDFT), as it has been successfully applied to optical excitations in atoms<sup>[31]</sup>. The application of this approach to X-ray absorption spectra at the L2,3 edges for the 3d transition metal series has been demonstrated recently <sup>[32]</sup>.

As for the experimental development, from 1930s to 1960, XAFS spectra were taken in transmission with low-power conventional X-ray tubes. Over the last three decades, the technique of XAFS has experienced a rapid development. This is primarily due to the application of synchrotron radiation (SR) which has a number of unique and excellent properties, such as high brilliance, wide and continuous wavelength, polarizability, and low emittance. In the 1970s, with the advent of the first dedicated synchrotron radiation sources using the 'white' synchrotron radiation of bending magnets <sup>[33]</sup> (i.e. SSRL), the data quality and the acquisition times for the XAFS spectra were greatly improved, although the spectra were allowed only for the investigation of the nearest neighbor distance and the local bonding geometry [34]. The first XAFS spectrum recorded on synchrotron radiation was measured by Stern et al. in 1974 [35], which signaled the beginning of rapid development in measurement techniques. A transmission technique utilizing a channel-cut monochromator and ion chamber was developed <sup>[36]</sup>, followed shortly by the fluorescence technique based on a solid-state detector for dilute systems [37], an energy-dispersive technique for time-resolved experiments [38] and an electron detection technique for surface-sensitive measurement <sup>[39]</sup>. In the second generation machine (e.g. BESSY I in 1987), the improvement in the signal-to-noise ratio and the more detailed fine structure of the oscillatory part opened the possibility to also investigate peaks in the Fourier transform at distances larger than the nearest neighbor distances, for example, in Ref. [27]. Furthermore, more attention was paid to the dynamics, as, for example, to the anisotropy of the surface Debye-Waller factors <sup>[40]</sup>. In the mid-1990s, when the third generation synchrotron radiation facilities (like ALS, APS, BESSY II, Elettra, ESRF, SPring-8) came into operation, insertion devices like wigglers and undulators started to be used routinely. These allowed for the measurement of XAFS with excellent statistics and high energy resolution. It is nowadays possible to record magnetic EXAFS (normally in the range of  $10^{-2} - 10^{-3}$  of the isotropic absorption), nearly free of noise with a detailed fine structure. Because of the high spectral purity, even small oscillatory fine structures in the X-ray absorption coefficient as, for example, the so-called atomic EXAFS can be identified by polarization-dependent surface EXAFS measurements. To date, more new XAFS techniques have been developed, such as time-resolved XAFS, micro-XAFS, and X-ray magnetic circular dichroism (XMCD), to meet more specific and critical demands in structural investigations.

#### 1.3 Outline

This review deals with the application of XAFS

to condensed matters. The basic principles of XAFS are single-scattering and multiple-scattering theories. The detailed data analysis procedure is also described, followed by a brief introduction of commonly used experimental techniques for recording an XAFS spectrum. Then certain examples of XAFS applications to semiconductors are reviewed, including thin films, quantum wells and dots, dilute magnetic semiconductors, and so on. Certain other XAFS-related techniques, such as *in situ* XAFS, micro-XAFS, quick-XAFS, and their applications in semiconductors, are also included. We have tried our best to include number of XAFS works in the research field of condensed matters, but it is difficult for us to reach this purpose well and to cover all the interesting and important studies.

### 2 Principles of XAFS

In this section, a simple physical description of the XAFS process and the basic EXAFS formula in the frame of single-scattering approximation will be given. The recently developed multiple-scattering theory will also be briefly described. The typical XAFS data analysis procedure will be outlined.

#### 2.1 Single-scattering theory

The absorption of X-ray by matter is a photoelectric process, in which an X-ray is absorbed by a core level (such as K, L,...) with a certain binding energy, and a photoelectron with wave number k is excited and out goes away from the absorbing atom. If there is a neighboring atom surrounding the absorbing atom, the excited photoelectron wave will be scattered back to the absorber by the electrons of the neighbor. The interference between the excited and scattered photoelectron waves thus give rise to the oscillation in the X-ray absorption coefficient: this is the origin of XAFS. Fig. 2 schematically describes this procedure.

In the framework of single scattering where the outgoing photoelectron wave is assumed to be scattered only once by the neighboring atoms, the oscillation part of the absorption coefficient  $\Delta \mu(E)$ , normalized to the atomic background  $\mu_0(E)$ , is given by<sup>[1]</sup>:

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$
  
=  $\sum_j \frac{N_j S_0^2 f_j(k)}{k} \times \int_0^\infty \frac{g(R_j)}{R_i^2} e^{-2r_j/\lambda(k)} \sin[(2kR_j + \delta(k) + 2\phi_c(k))] dR (1)$ 

where k is the photoelectron wave vector defined as k=  $[2m(E-E_0)/\hbar^2]^{1/2}$  and  $E_0$  is the threshold energy. For randomly oriented polycrystalline or solution samples, an isotropic average over angles must be performed. In this case the contributions from atoms of the same atomic number and at similar distances from the absorbing atom may not be resolvable from each other, and the atoms must be conceptually grouped together into "coordination shells" and  $N_i$  is the number of atoms in the *j*-th coordination shell. In Eq. (1),  $S_0^2$  is the amplitude reduction factor, R is the distance between the absorbing and scattering atoms,  $g(R_i)$  is the pair distribution function of the scattering atom,  $\lambda(k)$  is the mean free path of the excited photoelectron,  $f_i(k)$  and  $\delta(k)$  are the backscattering amplitude and scattering phase shift of the scattering atom, respectively, and  $\phi_{\rm C}(k)$  is phase shift of the absorbing atom.



**Fig.2** Pictorial view of the scattering of an outgoing wave by neighboring atoms.

Eq. (1) is the general EXAFS formula which is applicable to all systems with disorder degree from low to high. For low-disorder systems, the g(R) function can be represented by a Gaussian distribution:

$$g(R) = (2\pi\sigma^2)^{-\frac{1}{2}} \exp[-\frac{(R-R_j)^2}{2\sigma^2}]$$
(2)

then Eq. (1) is reduced to

$$\chi(k) = \sum_{j} \frac{N_{j} S_{0}^{2} f_{j}(k)}{k R_{j}^{2}} e^{-2k^{2} \sigma_{j}^{2}} e^{-2R_{j}/\lambda(k)} \times \sin[2k R_{j} + \delta(k) + 2\phi_{C}(k)]$$
(3)

Eq. (3) is also called the standard EXAFS formula, where  $\sigma^2$  (Debye-Waller factor) is the mean square variation in the distance *R*. The  $e^{-2k^2\sigma_j^2}$  term accounts for the effects of thermal vibration and structural dis-

order which smear out the EXAFS oscillations.

For a large disorder system, such as amorphous materials and liquid, the Gaussian distribution of the g(R) function fails. Instead the g(R) function can be modeled as a convolution  $P_G \otimes P_E$ , where  $P_G$  is a normalized Gaussian function centered at R = 0, and  $P_E$  is a weighted exponential distribution function:

$$P_{\rm E}(R) = \begin{cases} \frac{1}{\sigma_{\rm S}^{m+1}m!} (R - R_{\rm 0})^m \exp[-(R - R_{\rm 0})/\sigma_{\rm S}] & m = 0, 1, 2, \ R \ge R_{\rm 0} \\ 0 & R < R_{\rm 0} \ (4) \end{cases}$$

In this case, the EXAFS function (1) is expressed as:

$$\chi(k) = \sum_{j} \frac{N_{j} f_{j}(k) S_{0}^{2}(k)}{k R_{0j}^{2}} \exp\left(-2k^{2} \sigma_{t}^{2}\right) \times \left[1 + (2k \sigma_{s})^{2}\right]^{-(1+m)/2} e^{-2R_{0j}/\lambda(k)} \times \sin\left[2k R_{0j} + \delta_{j}(k) + 2\phi_{c}(k) + (m+1)\operatorname{actan}(2k \sigma_{s})\right] (5)$$

where  $R_0$  is the distance of the central atom to the closely packed atom,  $\sigma_8$  and  $\sigma_t$  are the structural (or statistic) disorder and thermal disorder, respectively. Eqs. (3) and (5) differ in that the  $e^{-2k^2\sigma_j^2}$  term in Eq. (3) is converted to  $exp(-2k^2\sigma_t^2) \times [1+(2k\sigma_8)^2]^{-(1+m)/2}$  in the amplitude and  $(m+1) \times actan(2k\sigma_8)$  is added in the phase shift.

#### 2.2 Multiple-scattering theory

The EXAFS Eq.(3) is derived based on the single-scattering approximation, which assumed that the final state of the photoelectron is modified by a single backscattering process of neighboring atoms. Clearly there are other cases if the photoelectron is scattered by more than one neighboring atom before returning to the absorbing atom. The single-scattering approximation is valid as long as the scattering is small. The addition of further scatterings, such as scattering from one neighbor to the next before interfering with the outgoing wave is sometimes important if the scattering is strong, especially in the low-k region for a low-Znearest neighbor. Practically, for extracting the structural information beyond the first shell by EXAFS, the consideration of multiple-scattering processes occurring in different shell atoms is often necessary. For collinear configuration, where three or more atoms are aligned or almost aligned, the multiple-scattering XAFS contributions can even be larger than the high shell single-scattering contribution.

Historically, the theoretical treatment of multiple-scattering EXAFS was first proposed by Lee and Pendry who classified the multiple-scattering contribution in terms of effective path length <sup>[6]</sup>. This approach takes the advantage of the Fourier transform in the EXAFS data analysis: since the interest lies in Fourier transforming the absorption coefficient to position space, at a given radial distance, only the multiple-scattering effects are considered, which contribute to the Fourier transform at this particular radius and neglect all the others. Its main advantages are its computational efficiency and accuracy; moreover, it provides a geometrical parameterization and interpretation of EXAFS, which is ideal for analyzing interatomic distances and other structural quantities. For example, the double scattering shown in Fig. 3 is characterized by the effective path length  $R_{\rm eff}$  =  $(R_1 + R_2 + R_3)/2$ . In general, these effective path lengths are long and involve successive large-angle scattering events. In k-space, they give rise to high frequency oscillations which tend to cancel out. The multiple scattering becomes important only in the low-k region where the electron free path becomes very long.



**Fig.3** Schematic plot of multiple-scattering path in which the photoelectron is scattered by two neighboring atoms.

A major advance in the path-by-path XAFS theory, which overcomes all the major computational difficulties of the multiple-scattering expansion, is based on a separable representation of the Green's-function propagators developed by Rehr and Albers <sup>[7, 8]</sup>. For an *N*-leg path  $\Gamma$  with scatterers at  $\mathbf{R}_1$ ,  $\mathbf{R}_2, \ldots, \mathbf{R}_N = \mathbf{R}_0$ , the result for the XAFS amplitude is:  $\chi_{\Gamma}(p) = \text{Im}\left\{S_0^2 \frac{e^{i(\rho_1+\rho_2+\rho_N+\dots+2\delta_1)}}{\rho_1\rho_2\cdots\rho_N}e^{-2\sigma_1^2p^2/2}\text{Tr}\left[M_iF^N\cdots F^2F^1\right]\right\}$ (6) where  $\boldsymbol{\rho}_i = p(\mathbf{R}_i-\mathbf{R}_{i-1}), p = (E-V_{\text{mt}})^{1/2}$  is the photoelec-

tron momentum measured with respect to the muffin-tin zero,  $F^i$  is the scattering matrix at site *i*,  $M_l$  is the termination matrix for the final state of angular momentum *l*. Finally, when  $k = (p^2 - k_F^2)^{1/2}$  is substituted, it is clear that the result for  $\chi_{\Gamma}$  can be recast exactly in terms of the standard XAFS Eq. (3), but with an effective scattering amplitude  $f_{\text{eff}}$ :

$$\chi_{\Gamma}(k) = \operatorname{Im}\left[\frac{f_{eff}(k)}{kR_{eff}^2} e^{i(2kR_{eff}+\delta_l(k))} e^{-2k^2\sigma^2}\right]$$
(7)

The implementation of these algorithms into the *ab initio* EXAFS code known as FEFF–named after the effective scattering amplitude  $f_{\text{eff}}$  in the theory has made accurate the high-order, multiple-scattering calculations of XAFS in general materials routine. By using FEFF code, the effective amplitude function  $f_{\text{eff}}$ , phase shift function  $\delta_l(k)$  and the mean free path of electrons  $\lambda(k)$  can be calculated for both single- and multiple-scattering paths.

#### 2.3 EXAFS data analysis

The aim of data analysis is to extract the structural information, such as interatomic distances, coordination numbers, disorder parameters and sometimes, types of atoms, in the various coordination shells for the "unknown" sample <sup>[1]</sup>. Interpretation of EXAFS data is normally based on the EXAFS Eq. (3). The standard data analysis procedure consists of the following steps: deglitching, pre-edge background removal; data normalization; conversion to *k*-space; Fourier transformation to *R*-space; inverse Fourier transform; and fitting procedure. The order of these steps is not critical and not all the steps are necessary. In the following the absorption spectrum of Cu foil is taken as an example to show the procedure in detail [41].

#### 2.3.1 Deglitching

The raw XAFS spectra often include sharp structures due to spurious reflections from the crystal monochromator or from the diffraction signals of the samples. These sharp structures are called "glitches" which may be many times larger than the EXAFS signal. These glitches may cause "spectral leakage" in the Fourier transform spectra; therefore it is often necessary to remove the worst glitches before further processing. The common deglitching technique is fitting the data on both sides of the glitch with a polynomial to interpolate through the glitch region.

#### 2.3.2 Pre-edge background removal

In analyzing the EAXFS data, the interest is only in the above-mentioned region and not the region below the absorption edge. The removal of the pre-edge background generally involves a fitting of the data before the edge to a certain functional form and extrapolating this function into the post-edge data. A traditional function used for the fitting is the Victoreen empirical formula  $\mu_v(E) = a E^{-3} + b E^{-4}$ .

The Victoreen formula is a good approximation for an in-laboratory EXAFS apparatus. However, for EXAFS spectra recorded in transmission mode on synchrotron radiation sources, caution should be exerted while using this formula. This is because in calculating the absorption coefficient  $\mu = \ln(I/I_0)$ , only a fraction of  $I_0$  (~ 20 %) is measured by the ion chamber. In order to compensate for this distortion, a modified Victoreen formula  $\mu_v(E) = a E^{-3} + b E^{-4} + c$  is often used instead (Fig. 4).



**Fig.4** A comparison of Victoreen function and its modified function.

#### 2.3.3 Data normalization

This step is taken to normalize the absorption coefficient to that of one single atom, for annihilating the difference in samples. There are two normalization methods: energy dependent and energy independent. For the energy independent normalization,

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu(E_0)}$$

Here,  $E_0$  is the energy point where the derivative  $d\mu(E)/dE$  is maximum, and  $\Delta\mu(E_0)$  is height of the step. A common method of determining the step is to fit the data within a few hundred eV below and above the edge with low-order polynomials, then extrapolate

them to the  $E_0$  point (Fig. 5). The difference between these two curves at  $E_0$  is the step  $\Delta \mu(E_0)$ .



Fig.5 The normalized data.

For the energy dependent normalization

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

a serious difficulty is that the atomic part of the absorption  $\mu_0(E)$  in general is neither measurable nor can it be calculated accurately. Practically, in order to obtain  $\mu_0(E)$ , a least squares cubic spline functions' fitting is used (Fig. 6). The data are divided into several regions, and separate cubic polynomials are fit to the data over each region. The cubics are constrained so that the values, the first and second derivatives match at the junctures (called "knots").



**Fig.6** The curve fitting of  $\mu_0$ .



For performing Fourier transform subsequently, the *E*-space EXAFS data  $\chi(E)$  must be converted to  $\chi(k)$  in the wave vector *k*-space. This is easily done according to

$$k = \sqrt{2m(E - E_0)/\hbar^2}$$

At the same time, the  $\chi(k)$  data are generally weighted with some power of  $k^n$  (n = 1, 2, 3) to compensate for the decay of the waves with extended k(Fig. 7).



**Fig.7** The curve of  $k^3\chi(k)$  as a function of *k*.

#### **2.3.5** Fourier transformation to *R*-space

The next important step in the analysis is Fourier transforming the  $k^n$ -weighted  $\chi(k)$  function to the position *R*-space (Fig. 8). Since the Fourier transform requires a uniform grid in *k*-space, before the transformation one should interpolate the experimental data in an even grid *k*-space. The grid in EXAFS analysis is commonly  $\Delta k = 0.05$  Å<sup>-1</sup>. The *R*-space spectrum indicates the radial distribution of the neighbors where the contributions of the different shells of the neighbors are isolated.



**Fig.8** Fourier transforming the  $k^3\chi(k)$  function to the *R*-space.

#### **2.3.6** Reverse Fourier transform

The following step inversely transforms the R-space peak corresponding to a single shell to k-space (Fig. 9). Then the oscillation of this specific shell is filtered from the overall spectrum, which allows the extraction of the structural information of the shell through a fitting procedure.

2.3.7 Fitting procedure

Once the single-shell oscillation has been isolated, the quantitative structural parameters can be obtained through a fitting procedure according to the EXAFS basic formula Eq. (3). Before doing so, the amplitude and phase-shift functions should be known. These functions can be determined experimentally from the model compound by either fitting or ratio method, or from theoretical calculations or tabulated values. Thanks to the development of the accurate *ab initio* calculations of FEFF code, nowadays the theoretical amplitude and phase-shift are more routinely used than the experimental ones.



**Fig.9** Inversely Fourier transforming the single shell peak to *k*-space.

There are various algorithms for fitting the filtered experimental EXAFS  $\chi(k)$  function, among which the least squares algorithm is most commonly used. However, the least squares algorithm suffers certain drawbacks, for example, many local minima in the sum of squares function may exist, and the obtained structural parameters are often physically impossible. To overcome this problem, certain new algorithms, such as simulated annealing method have been developed. As an example, Table 1 summarizes the structural parameters of Cu foil extracted from EX-AFS fitting using the USTCXAFS3.0 software package which implements the simulated annealing method.

Table 1 The structure parameters of Cu foil from a curve fitting

Parameter	Experimental value	Fitting result
<i>R</i> / Å	2.55	2.55
Ν	12.0	12.0
$\sigma$ /Å		0.086
$E_0$	0.0	-4.4

## **3** XAFS experimental techniques

The magnitude of XAFS absorption coefficient  $\mu(E)$  is typically on the order of  $10^{-2}$  of the total absorption. This requires a fairly precise and accurate measurement. The main experimental challenges are obtaining a high photon flux X-ray source that can be tuned in energy, and high-quality detectors for recording the XAFS data. The X-ray source typically used is

synchrotron radiation, which provides a full range of X-ray wavelengths with high brilliance. By using a monochromator, a particular energy can be selected. Depending on the different schemes of detecting  $\mu(E)$ , various XAFS experimental modes have been developed. Among them, the transmission and fluorescence modes are the most frequently used and will be briefly described.

#### 3.1 Transmission XAFS

The first mode used for collecting XAFS is the transmission mode, where a monochromatized X-ray passes through a sample, as shown schematically in Fig. 10. The incident and transmitted beam intensities  $I_0$  and I are measured using two ion chambers as a function of the photon energy, and the absorption coefficient is  $\mu(E) = \ln(I/I_0)$ . Care must be taken to make sure that the two ion chambers work in the linear region.



Fig.10 The schematic XAFS experiment in a transmission mode.

For concentrated samples in which the element of interest is a major component, XAFS should be measured in transmission. In order to get a proper signal for *I*, the sample thickness must be optimized. Typically, the sample thickness *d* should be adjusted so that the edge jump  $\mu d \approx 1$ . For Fe metal, this gives  $d = 7 \mu m$ , while for many solid metal oxides; *d* is often tens of microns. For dilute solutions, sample thickness is typically in the millimeter range.

In addition to requiring the right thickness for transmission measurements, the sample must be uniform, and free of pinholes. For a powder, the grain size cannot be much bigger than an absorption length. If these conditions can be met, excellent XAFS spectra can be easily obtained by transmission measurements. This method is usually appropriate for model compounds, and elements with concentrations > 10 %.

#### 3.2 Fluorescence XAFS

In a transmission experiment for a dilute sample,

the thickness of the sample has to be adjusted so that the edge jump  $\mu d \approx 1$ , but the transmitted beam intensity is exponentially attenuated and the signal-to-noise ratio rapidly decreases. In this case, monitoring the X-ray fluorescence is more preferred, since the fluorescence yield is proportional to the absorption efficient. In a fluorescence XAFS measurement, the X-rays emitted from the sample will include the fluorescence line of interest, fluorescence lines from other elements in the sample, and both elastic and inelastic (Compton) scattering X-rays.

To make good fluorescence XAFS measurements, it is necessary to collect as much of the available signal as possible. Although in general the fluorescence is emitted isotropically, the scatter is not emitted isotropically because the X-rays from a synchrotron are polarized in the plane of the synchrotron. This means that elastic scatter is greatly suppressed at 90° to the incident beam, in the horizontal plane. Therefore, fluorescence detectors are normally placed at a right angle to the incident beam, and the sample is at 45° to both the incident beam and the fluorescence detector, as shown schematically in Fig. 11.



 $\label{eq:Fig.11} {\mbox{ Fig.11 } } {\mbox{ The schematic XAFS measurement in a fluorescence mode.} }$ 

The fluorescence yield for a small thickness limit is

$$I_{\rm f} = I_0 \varepsilon_{\rm f} (\frac{\Omega}{4\pi}) \frac{\mu_{\rm A}(E)}{\mu_{\rm T}(E_{\rm f}) + \mu_{\rm b}(E) + \mu_{\rm A}(E)}$$
(8)

where  $\varepsilon_f$  is the fluorescence efficiency,  $\Omega/4\pi$  is the solid angle of the detector,  $E_f$  is the energy of the fluorescent X-ray,  $\mu_A(E)$  is the absorption from the element of interest,  $\mu_b(E)$  is the background absorption coefficient of all the other elements, and  $\mu_T(E_f)$  is the total absorption coefficient at the fluorescent X-ray energy. If  $\mu_T(E_f) + \mu_b(E) >> \mu_A(E)$ , Eq. (8) reduces to  $I_{\rm f} \propto I_0 \ \mu_{\rm A}(E)$ , and

$$\mu_{\rm A}(E) \propto \frac{I_{\rm f}}{I_0} \tag{9}$$

In fluorescence mode, it is necessary to collect only the intensity of the fluorescence lines of interest, and completely suppress the scatter peak and other fluorescence lines. This would greatly suppress the background intensity, and increase the signal-to-noise ratio. One can reduce the intensity of the scattering by one order of magnitude by inserting an X-ray filter which has the absorption edge between the characteristic line and the elastic scattering peak. Conventionally, a thin metal foil or a homogeneous powder containing the Z-1 element is used as a filter. To avoid reradiation from the filter itself, a set of slits (Soller slits) is often used to preferentially collect emission from the sample and block the emission from the filter.

## 4 XAFS applications

#### 4.1 IV semiconductors

## **4.1.1** Ge/Si thin films

It has been well accepted that a clean Si(001) surface shows a  $(2 \times 1)$  reconstruction and shortened interatomic distance than the counterpart in bulk Si. For Ge overlayers grown on Si(001), the formation of the dimmer and the interatomic distance are more complicated, depending on the number of Ge<sub>n</sub> overlayers. Oyanagi *et al.* studied *in situ* the local structure of Ge epitaxial overlayers by fluorescence XAFS in the grazing incidence geometry <sup>[42]</sup>. The samples with Ge thickness from 1 to 4 monolayers (ML) were grown by molecular beam epitaxial (MBE) on Si(001) substrate at 400 °C.

Fig. 12 shows the Fourier filtered first-shell Ge *K*-edge EXAFS oscillations and the calculated curves of model structure for 1–4-ML Ge on Si(001)<sup>[43]</sup>. The Ge-Si and Ge-Ge bond lengths for 1-ML Ge on Si(001) were determined by a least squares fit using empirical total phase-shift and theoretical backscattering amplitude. The effective coordination number  $N_{\text{Ge}}^*$  and  $N_{\text{Si}}^*$  calculated for model dimmer structures were treated as constants. The obtained Ge-Ge distance is 2.51 ± 0.01 Å and Ge-Si distance is 2.40 ± 0.01 Å for 1-ML Ge on Si(001), indicating that 1-ML Ge overlayer on Si(001) forms an elongated dimmer structure. It is interesting

that the Ge-Ge distance is significantly longer than the interatomic distance 2.45 Å in Ge bulk, in spite of the uniaxial strain due to lattice mismatch which should shorten the bond length within a simple elastic deformation model. These bond length values remain almost unchanged within  $\pm$  0.01 Å for 2-ML Ge on Si(001). However, upon increasing the number of  $Ge_n$ overlayers to n=4, the Ge-Ge distance is reduced to  $2.47 \pm 0.01$  Å and the Ge-Si distance is  $2.38 \pm 0.01$  Å. Fig. 13 shows the surface strain in 1-ML and 2-ML Ge on Si(001) schematically. Stress components are indicated by directions of the arrows. Strains are induced by surface reconstruction (dimmer strain) and atomic size effect (mismatch strain). A possible channel of atomic migrations is indicated by arrows in the bottom figure.



**Fig.12** The first-shell EXAFS oscillations and the calculated curves of model structure for 1-4-ML Ge on Si(001).



**Fig.13** The schematic surface strain in 1-ML and 2-ML Ge on Si(001).

#### 4.1.2 Strained-layer superlattice

Artificially ordered GeSi superlattices possessing electrical and optical properties have opened a doorway to band-structure engineering through heterostructures formed by the strained-layer coherent epitaxy of Si and Ge. The (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub> monolayer strained-layer superlattice grown on Si(001) substrate, has shown strong optical transitions (0.75, 1.25, 2.31 eV) unique to the superlattice period <sup>[44]</sup>, which are found neither in constituent crystals nor in the Ge<sub>0.5</sub>Si<sub>0.5</sub> alloy. Quantitative calculations of optical transition require direct information on structural parameters for GeSi strained superlattice, not only in crystallographic but also in local structural viewpoints. By using grazing incidence fluorescence XAFS, Wei et al. studied the local structure of the (Ge4Si4)5 monolayer strained-layer superlattice <sup>[45]</sup>.

Fig. 14 shows the normalized Ge K-edge EXAFS oscillations  $\chi(k)$  for (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub>, crystalline Ge (c-Ge) and  $Ge_xSi_{1-x}$  alloys. EXAFS spectra for both (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub> and  $Ge_{0.5}Si_{0.5}/Si(001)$  have an intermediate profile suggesting that these two samples are characterized by an almost equal amount of Ge and Si scatterers. The first shell peak in the Fourier transform of the  $k\chi(k)$ was inversely transformed into a k space to isolate its contribution. The least squares curve fitting was used to fit the filtered EXAFS oscillations. The best-fit bond lengths for (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub> are  $R_{\text{Ge-Ge}} = 2.42 \pm 0.01$  Å and  $R_{\text{Ge-Si}} = 2.38 \pm 0.01$  Å. The coordination numbers are  $N_{\text{Ge}} = 1.8$  and  $N_{\text{Si}} = 2.2$ , respectively. The bond length  $R_{\text{Ge-Si}} = 2.38$  Å in (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub> is identical with the value for the dilute Ge atoms doped into Si crystal, suggesting that the bond-length compression takes the upper limit of isotropic deformation. The observed  $R_{\text{Ge-Ge}}$  and  $R_{\text{Ge-Si}}$  values take slightly larger values than the calculated values for model (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub> superlattice. The overestimation of bond-length compression may occur since most of the model structures do not take interface mixing and nonuniform longitudinal displacement into account. Based on these results, it may be concluded that the lattice matching is achieved by tetragonal deformation by bond bending but the Ge layer is highly compressed.

Fig. 15 shows the schematic structures for  $(Ge_4Si_4)_5$  with an ideal Ge/Si interface (left) and with an interface mixing (right). In the latter model, the Ge

overlayer is assumed to have 0.5 ML site exchange upon deposition and 1 ML segregation upon Si overlayer growth. Fig. 15(b) shows the schematic presentations of the interface local structure for the first Ge layer deposited on Si(001) with and without a site exchange effect. Fig. 15 (a) shows the ideal interface while (b)–(d) are model interface structures where 0.5 ML Ge sites exchange with Si atoms. Note that the site exchange decreases the  $N_{Ge}/N_{Si}$  ratio depending on which sites are involved, although (c) and (d) give the same value.



**Fig.14** The EXAFS  $\chi(k)$  function for (Ge<sub>4</sub>Si<sub>4</sub>)<sub>5</sub>, crystalline Ge (c-Ge) and Ge<sub>x</sub>Si<sub>1-x</sub> alloys.



**Fig.15** The schematic structures for  $(Ge_4Si_4)_5$  with an ideal Ge/Si interface (left) and with an interface mixing (right).

#### **4.1.3** Ge/Si(001) quantum dots

The self-assembled Ge/Si quantum dots (QDs) is also an interesting research topic. Although the Stranski-Krastanov (S-K) mode are commonly used to describe the growth of Ge QD on Si, due to the intermixing between Ge and Si, the real formation of Ge QDs is much more complicated. Moreover, the capping of the Ge islands by Si, which is necessary to avoid oxidation, is also likely to modify the morphology, structure, electronic, and optical properties of Ge QDs <sup>[46]</sup>. A simultaneous determination of their strain and composition is of interest. Sun *et al.* first used the MS-EXAFS method to study the local structures around Ge atoms in the first three coordination shells for self-assembled Ge QDs grown at 510 °C, then capped by Si at different temperatures (300 and 510 °C) <sup>[47]</sup>. The results provide straightforward proof regarding different degrees of Ge/Si intermixing at different capping temperatures and reveal the strain status of the Ge-Ge bonds within three coordination shells in the Ge QDs.

The authors first performed a preliminary fitting on the data of c-Ge using all 10 scattering paths in the first three shells. It was found that the experimental EXAFS data for the diamond structure can be well reproduced by considering only the single-scattering paths and an additional dominant MS path  $Ge_0 \rightarrow B_1$  $\rightarrow$  B<sub>2</sub>  $\rightarrow$  Ge<sub>0</sub> (DS2). Based on this, and assuming a suitable structure model (Fig.16), EXAFS contributions from the environments around Ge in the islands and the wetting layer are separated. The fitting done in *R*-space for the first three shells is shown in Fig. 17. From the coordination numbers and considering the interface effect, the average Ge concentrations in the islands are estimated to be ~ 0.9 and ~ 0.4 for the QDs capped at 300 and 510 °C, respectively. It is unambiguously demonstrated that in the capping process much stronger Ge/Si intermixing occurs at the temperature of 510 °C than at 300 °C. For the Ge dots capped by Si at 300 °C, from the first shell bond lengths  $R_{\text{Ge-Ge}}$  (2.43 Å) and  $R_{\text{Ge-Si}}$  (2.37 Å) as well as the estimated in-plane and out-of-plane bond angle distortion  $\Delta\theta$  (-2.0°) and  $\Delta\theta'$  (1.0°) by the elastic theory, the local strain in the nearest neighbor around Ge is mainly accommodated by the bond bending. The observed Ge-Ge interatomic distances of the second  $(3.93 \pm 0.03 \text{ Å})$  and third  $(4.61 \pm 0.04 \text{ Å})$  shells in the islands are  $0.07 \sim 0.08$  Å shorter than the corresponding values in c-Ge, indicating the accommodation of compressive strain by stretching the higher shell Ge-Ge bonds. This implies that the mismatch strain in the Ge core of the QDs appears mainly in the second and higher Ge-Ge shells. For Ge dots capped at 510 °C, Ge is strongly intermixed with Si, but the local

structure of the compressively strained pure Ge phase in the core of Ge QDs is hardly changed.



**Fig.16** Schematic cross-sectional geometry of the Ge islands and the Ge wetting layer grown on Si (001).



**Fig.17** The radial structural function by Fourier transforming  $k^2\chi(k)$  functions: experiment (solid) and MS fit (open circle).

## 4.2 III-V and II-VI Dilute magnetic semiconductors

#### 4.2.1(Ga, Mn)N

Diluted magnetic semiconductors (DMS) materials are an important candidate for future technological applications in spintronics. Mn-doped GaN is theoretically predicted to have a high Curie temperature  $T_{\rm C}$ exceeding room temperature <sup>[48]</sup>, stimulating numerous attempts to synthesize this promising DMS material. In order to understand how Mn atoms affect the properties of (Ga,Mn)N films, the local structure around Mn in (Ga,Mn)N films is studied using Mn *K*-edge EXAFS <sup>[49]</sup>.

Two cubic  $Ga_{1-x}Mn_xN$  films (x=0.025 for sample A and x=0.10 for sample B) with layer thickness of about 0.3 µm were grown on GaAs(001) substrate at 700 °C under nitrogen-rich conditions by plasma-assisted MBE. Hall-effect measurements showed that the as-prepared  $Ga_{1-x}Mn_xN$  samples have *p*-type conductivity, with the hole density of about  $5 \times 10^{17}$  cm<sup>-3</sup>. X-ray diffraction (XRD) studies demonstrated that they have cubic zinc-blende structure.

Fig. 18 shows the Fourier transform of EXAFS  $k^{3}\chi(k)$  for samples A and B. For sample A, a curve fitting on peak A and B was performed using the backscattering amplitude and phase-shift functions calculated by FEFF7 code. Peak A corresponds to the nitrogen nearest neighbors surrounding Mn impurities with a coordination number 3.4 at distance 2.00 Å. Peak B is actually a composite peak consisting of about 12 Ga and 12 N neighbors at distances 3.22 and 3.93 Å, respectively. Comparing with the Ga-N bond length 1.93 Å in cubic GaN, the Mn-N bond in sample A is elongated. This is reasonable considering a large number of nitrogen defects. For sample B, an additional peak D between peak C and peak E, is obviously apparent. This peak is absent for sample A. This indicates that there must be certain other Mn related structures contributing to the Fourier transform of sample B between distances of 2.00-3.22 Å. The ideal model, in which Mn impurities are substituted into the Ga sites randomly in GaN lattice, is no longer suitable. Kinds of simulations of sample B have been made. The results in Fig. 19 indicate that only the model containing substitutional Mn, interstitial Mn, and Mn clusters can best reproduce the features of sample B, indicating that the formation of Mn clusters and interstitial Mn impurities is mostly possible for heavily doped  $Ga_{1-x}Mn_xN$  (x = 0.10) films.



**Fig.18** Fourier transforms of the experimental Mn *K*-edge EXAFS  $k^3\chi(k)$  functions (fine lines) for samples A and B compared with the fitting result of sample A (thick line).



**Fig.19** Magnitude of Fourier transform of EXAFS  $k^3\chi(k)$  and various simulation results of sample B.

#### **4.2.2** (Ga, Mn)As

Local structures around Mn in another important DMS material,  $Ga_{1-x}Mn_xAs$  (x=0.005, 0.074) films, have also been studied using Mn *K*-edge EAXFS <sup>[50]</sup>. The samples were grown on GaAs(001) substrates at 250–300 °C under As-rich conditions. The thickness of the films is about 1 µm. The RHEED patterns during the growth and XRD showed that the structure of the films is a single phase of zinc-blende type. The EXAFS spectroscopy of the samples were measured with the fluorescence detection mode using a 19-element solid-state detector. As a reference, EXAFS spectrum of the NiAs-type MnAs bulk powder was measured in the transmission mode.

The Fourier transform of EXAFS  $k\chi(k)$  for  $Ga_{1-x}Mn_xAs$  and MnAs samples are shown in Fig. 20, where the bottom two lines are the calculated results of two model structures, a NiAs-type MnAs model, and a substitutional Mn model, in which the Mn atoms replace the Ga atoms of the GaAs lattice without any modification of the GaAs lattice. The calculated results for both structures show the peaks of the nearest-neighbor As atoms and two peaks of the farther atoms. Although the position of the nearest-neighbor As atom in  $Ga_{1-x}Mn_xAs$  is almost the same as that in MnAs, the second and third peaks in  $Ga_{1-x}Mn_xAs$  are similar to those for the substitutional Mn model. The obtained Mn-As bond length (2.49-2.50 Å) in  $Ga_{1-x}Mn_xAs$  from curve fitting, is 2 % larger than the Ga-As bond length (2.44 Å) in bulk GaAs. In the second Ga and third As shells, the interatomic distances in  $Ga_{1-x}Mn_xAs$  are the values expected for bulk GaAs. This indicates that the Mn atoms in  $Ga_{1-x}Mn_xAs$  are

substituted into the Ga sites and induce an elongation of the bond between the Mn atoms and the nearest-neighbor As atoms, which causes statistical disorder of the higher shell atoms.



**Fig.20** Fourier transform of experimental (fine lines) EXAFS  $k\chi(k)$  compared with the fitting results (bold lines).

The situation of  $Ga_{1-x}Mn_xAs$  is opposite to that of the zinc-blende type  $In_{1-x}Mn_xAs^{[51]}$ , in which the In-As bond length (2.61 Å) of the host InAs lattice is larger than the expected Mn-As bond length (2.55 Å). Therefore in local structures of DMS's, the bond around the low-composition magnetic ions is compressed or elongated depending on the host material structure, and this bond anomaly is limited to the nearest-neighbor atoms.

#### **4.2.3** (Zn, Co)O

Magnetic ions-doped ZnO is another semiconducting material which is theoretically predicted to have room-temperature ferromagnetism. In the case of Co-doped ZnO system, although ferromagnetic behavior with the Curie point higher than 280 K were reported <sup>[52, 53]</sup>, there were two contrary opinions regarding the origin of this room temperature: intrinsic ferromagnetic behavior or extrinsic phenomenon caused by the presence of Co clusters. In order to clarify this issue, EAXFS studies on two types of Co-doped ZnO thin films were performed <sup>[54]</sup>. The first type is Co-doped thin films ( $Zn_{1-x}Co_xO$  with  $x \le 0.12$ ) in which  $Co^{2+}$  ions atomically substitute for  $Zn^{2+}$  ions. The second type corresponds to the thin films containing nanometer-sized Co-metal clusters. Both the magnetization-temperature curve and the magnetization-field curves demonstrated that the first type of films were paramagnetic, while the second type showed room-temperature ferromagnetism.

Fig. 21 compares the Fourier transform amplitude of the pure ZnO film at the Zn *K*-edge EXAFS data, with that of Zn<sub>0.9</sub>Co<sub>0.1</sub>O film from the Co *K*-edge spectrum. It indicates that the results of the two films are very similar to each other. The interatomic distances for the two major peaks (1.55 and 2.90 Å) of the undoped ZnO film are essentially the same as those of the Zn<sub>0.9</sub>Co<sub>0.1</sub>O film. Thus, the EXAFS results clearly indicate that Co atoms atomically substitute for Zn atoms, without forming Co metal clusters or Co-containing oxide precipitates. The ferromagnetism in Co-doped ZnO films for  $x \le 0.12$  is not relevant to the carrier-induced RKKY mechanism.



**Fig.21** Fourier transform amplitude of Zn *K*-edge EXAFS data for ZnO film and Co *K*-edge EXAFS data for  $Zn_{0.9}Co_{0.1}O$  film.

Fig. 22 compares the Co *K*-edge EXAFS results of Co-doped ZnO films (x=0.15 and 0.20) with those of Co-metal foil and CoO. It can be seen that for Zn<sub>1-x</sub>Co<sub>x</sub>O films with  $x \ge 0.12$ , the Co-metal clusters, not CoO-type oxide clusters, are formed in Co-doped ZnO films by the annealing in a reduced oxygen partial pressure at 600 °C. The observed ferromagnetism for this type of Zn<sub>1-x</sub>Co<sub>x</sub>O films originates from the nanometer-sized Co clusters.

## 4.3 In situ XAFS

#### 4.3.1 Liquid Ge

Structural investigations on liquid Ge (*l*-Ge) are of fundamental interest in the understanding of microscopic atomic interactions. Upon melting ( $T_m$ =1210.4 K), Ge undergoes a semiconductor-to-metal transition. Its conductivity jumps by a factor of 11, its density increases by 5 %, and its structure goes from an open



**Fig.22** Co *K*-edge EXAFS results of several Co-containing specimens.

diamond lattice with coordination number of 4 to a more compact liquid structure characterized by a coordination number between 6 and 7. In order to understand the complex interplay between the covalent and metallic bonding character in *l*-Ge, Filipponi *et al.* measured eight independent Ge *K*-edge XAFS spectra for *l*-Ge from about 950 K in highly supercooled condition up to 1610 K <sup>[55]</sup>.

The difficulties in interpreting EXAFS data from liquid systems mainly arise from the strong asymmetry of the first g(r) peak that continuously merges into the long distance tail. A preliminary interpretation of the EXAFS from liquid matter is given by using the equation:

$$\chi(k) = \int_0^\infty 4\pi \, r^2 g_2(r) \, \gamma^{(2)}(r,k) \mathrm{d}r$$

where the  $\gamma^{(2)}(r, k)$  function is the EXAFS single-scattering signal of atom at distance *r*.

As a starting model, a g(r) function from molecular dynamical (MD) simulation <sup>[56]</sup>, which was decomposed into a first asymmetric peak plus a long-distance tail, was used. It turned out that this g(r)function cannot well reproduce the experimental EX-AFS spectra of *l*-Ge, especially in the low-*k* and high-*k* region. Alternatively, two  $\Gamma$ -function components were used to fit the first shell peak. The refined g(r) models for *l*-Ge at eight different temperatures are shown in Fig. 23. The two peaks account for about 1.8 and 5.0 atoms, respectively. Fig. 24 magnifies certain g(r) functions in Fig. 23. The maximum of the g(r)decreases from 2.30 in the supercooled liquid at 950 K, to about 2.00 in the liquid just above  $T_{\rm m}$ , and down to 1.83 in the high-temperature liquid at 1610 K. Simultaneously to the peak-height decrease, an overall broadening of the shape and a shift of the low-*r* edge toward shorter distances are observed. However, the position of the maximum of the *l*-Ge g(r), 2.62  $\pm$  0.02Å, is found to be independent of the temperature. These results are in excellent agreement with the *ab initio* MD results <sup>[56]</sup>, neutron diffraction data <sup>[57]</sup>, and energy-dispersive XRD results <sup>[58]</sup>. This suggested that the reliable EXAFS experiments could complement the well-established diffraction technique for studying liquid systems with a certain number of experimental advantages.



**Fig.23** Refined g(r) models for *l*-Ge at eight different temperatures.



**Fig.24** Comparison between 4 refined g(r) functions corresponding to 950, 1050, 1230, and 1610 K.

#### 4.3.2 Liquid InSb

The studies on the structures and properties of molten matters have attracted wide interest, since it is not clear enough for certain fundamental problems in liquid physics. Upon melting III-V semiconductors with zinc-blende structure have exhibited certain special properties, such as that the covalent bonds are destroyed, the density increases and a semiconductor-metal transition occurs. Wei *et al.* conducted *in situ* XAFS study to probe the local structures of the premolten and liquid InSb compounds <sup>[59]</sup>.

Fig. 25 demonstrates the In and Sb *K*-edge EX-AFS functions  $k\chi(k)$  of the premolten and liquid InSb (*l*-InSb) compound (solid lines). Compared with that of the premolten InSb (723 K), the oscillation intensity of *l*-InSb at 828 K ( $T_m$ =798 K) in the high *k* region further decreases. Moreover, the oscillation intensity of the In *K*-edge EXAFS functions in the high *k*-range drops faster than that of the Sb *K*-edge EXAFS functions. These results indicate that during the solid-liquid transition, the local structures around Sb and In atoms change markedly and the disorder degree around In atoms is slightly larger than that of Sb atoms for *l*-InSb.



**Fig.25** The RMC fitting results for (a) In and (b) Sb *K*-edge  $k\chi(k)$  EXAFS functions of InSb at room temperature, pre-molten InSb (723 K) and *l*-InSb (828 K): experiment (solid line), fitting (open circle).

A model-independent method of reverse Monte Carlo (RMC) calculations was used to simultaneously fit both In and Sb *K*-edge EXAFS functions  $k\chi(k)$ . The fitting results indicate that the average bond length  $R_1$ (2.80 Å) and the average coordination number  $N_1$  (4.0) of the first In-Sb (or Sb-In) shell of pre-molten InSb (723 K) are similar to those (2.79 Å, 4.0) of crystalline InSb at 300 K with a zinc-blende structure. For the

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*l*-InSb (828 K), the  $R_1$  and  $N_1$  of the first In-Sb shell are 2.90 Å and 5.8, and the  $R_1$  and  $N_1$  of the first Sb-In shell are 2.90 Å and 5.5, respectively, and few percent of In-In (or Sb-Sb) coordination appears in the first shell. It implies that the tetrahedron structures of the In-Sb (or Sb-In) covalent bonds of InSb compound have been destroyed in the liquid state.

#### 4.4 Micro-XAFS and quick-XAFS

### 4.4.1 (Ga,Mn)N DMS by micro-XAFS

For growing room-ferromagnetic (Ga,Mn)N DMS materials, low-temperature crystal growth methods like MBE are mostly used. However, due to the solubility limit of Mn ions in GaN host material, when a high Mn concentration is introduced, formation of secondary phases as well as metallic clusters occur easily. Analytical probes with high sensitivity to identify these defects are in extreme demand. Martínez-Criado *et al.* applied synchrotron microprobe based on XANES imaging with micron resolution to detect metallic Mn in GaN <sup>[60]</sup>. This valuable instrument is capable of quantifying and mapping mixed valence state samples with high spatial resolution, elemental sensitivity, and chemical speciation.

The GaN samples with Mn concentrations ranging from 0.05 % up to 11 % were grown by low temperature plasma-assisted MBE. Scanning  $\mu$ -X-ray fluorescence (XRF) and XANES measurements were carried out at the ID21 and ID22 X-ray microprobe beamlines of the European Synchrotron Radiation Facility (ESRF). The monochromatic beam of ID21 beamline was focused on the sample to a spot of 0.6  $\mu$ m × 0.9  $\mu$ m size with a focus depth of ~ 0.4 mm by means of Au Fresnel zone plates as focusing lenses. At the ID22 beamline, the hard X-ray monochromatic beam was focused on the sample to a spot of 1.5  $\mu$ m × 3.5  $\mu$ m size with a focus depth of 300  $\mu$ m by Kirkpatrick-Baez mirrors.

In order to study the distribution and partitioning of Mn atoms on the micrometer scale in specific valence states, oxidation state mapping has been performed. In this approach, two-dimensional X-ray fluorescence maps are taken at preferential monochromatic energies, which excite different Mn oxidation states. Fig. 26 shows the XRF images obtained by measuring the Mn  $K_{\alpha}$  line intensities at different excitation energies. It is evident that for the sample with lowest Mn content (0.05 %), Mn element is distributed homogeneously on the micrometer scale for all the chosen energies. On the contrary, for the highest Mn concentration (11 %), Fig. 26 reveals different Mn patterns as a function of the incident energy. The basic principle of chemical imaging is to express the Mn K-edge XANES data in each pixel  $\mu_{Mn}$  at each energy E as a summation over all different Mn valencies k. An image fitting algorithm was used to decompose the XANES images into different oxidation state distributions. For GaN samples with lower Mn content, a preferential homogeneous distribution of mixed Mn<sup>2+</sup> and Mn<sup>3+</sup> states was observed rather than metallic Mn centers. For the highest Mn-doped GaN sample, the resulting valence state maps are shown in Fig. 27. The intensity scales clearly show Mn<sup>2+</sup> as the dominant center, accompanied with Mn<sup>0</sup> in a lesser degree, and almost no signal from Mn<sup>3+</sup>. The Mn<sup>0</sup> pattern suggests the presence of specific cluster-like features, indicating surface segregation of metallic Mn centers.



**Fig.26** XRF images obtained by measuring the Mn  $K_{\alpha}$  line intensities at different excitation energies.



Fig.27 Mn oxidation state maps of the highest Mn-doped GaN sample containing  $Mn^0$ ,  $Mn^{2+}$ , and  $Mn^{3+}$  centers.

#### 4.4.2 Liquid Ge probe by Q-XAFS

Pascarelli *et al.* investigated the local structure of undercooled liquid Ge (*l*-Ge), by means of time-resolved XAFS <sup>[61]</sup>. Hundreds of Ge *K*-edge XAFS spectra were recorded during a rapid cooling of the melt, on the beamline ID24 of ESRF. The spectra were collected at 1.2 s intervals and the acquisition time per spectrum was 520 ms. Another series of 500 scans, concerning a 60-eV energy range around the Ge K-edge absorption jump, were recorded at the same cooling rate, in order to have a finer mesh in the edge temperature evolution. These scans were again collected at intervals of 1.2 s and the total acquisition time/scan was 120 ms.

The upper panel of Fig. 28 shows the measured energy shifts  $\Delta E$  of the absorption edge as a function of temperature during a heating/cooling cycle at a constant rate of 1.7 K·s<sup>-1</sup>. During the heating ramp, the abrupt step in  $\Delta E$  at  $T_1$  is associated to the melting of the sample ( $T_m$ =1210 K), indicating that melting occurs almost simultaneously for all the Ge micrometric grains. On the other hand, upon freezing, a less abrupt step in  $\Delta E$  is observed reflecting the statistical nature of the nucleation process on the large ensemble of droplets. The energy shift starts around a temperature value  $T_2 \sim 850$  K. The temperature range during which the metastable undercooled liquid is probed is  $\Delta T_u = T_1 - T_2 = 360 \pm 5$  K.



**Fig.28** Upper panel: Measured edge shift values  $\Delta E$  as a function of temperature during a heating/cooling cycle. Lower panel: Maximum amplitude of the first peak in the Fourier transform P1(S) as a function of temperature.

Fig. 29 displays the amplitude of Fourier transforms (FT) of the XAS spectra collected during the cooling ramp. The FT of the *l*-Ge presents a weak structure S at a position similar to that of the first peak in crystalline Ge. As the temperature decreases below  $T_{\rm m}$  the main features in the FT of the *l*-Ge remain apparently unchanged, until the onset of nucleation where two important modifications appear: (a) the amplitude of S increases very rapidly and forms a well-defined peak P<sub>1</sub> and (b) another peak P<sub>2</sub> corresponding to the second-neighbor coordination shell rises. This latter reflects the detection by XAS of tetrahedral configurations, that is, the formation of crystalline grains. In order to compare the temperature dependence of the structure to that of the electronic state, the lower panel of Fig. 28 shows the variation of the amplitude of P<sub>1</sub> (S) as a function of *T*: the amplitude is very weak for T > 850 K and increases abruptly close to  $T \sim 850$  K. A comparison with the upper panel shows that the crystallization and the metalsemiconductor transition occur simultaneously.



**Fig.29** Amplitude of Fourier transforms of the XAS spectra collected during the cooling ramp.

### 5 Outlook and perspective

XAFS has been developed into a mature technique with numerous applications in physics, chemistry, materials science, biology, and environmental science. The recent significant advances in theory, experimental methods, and data analysis have extended this technique to more extensive fields. With new generations of synchrotron radiation sources coming online and more novel XAFS beamline becoming available, the range of application of XAFS will be further extended.

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