

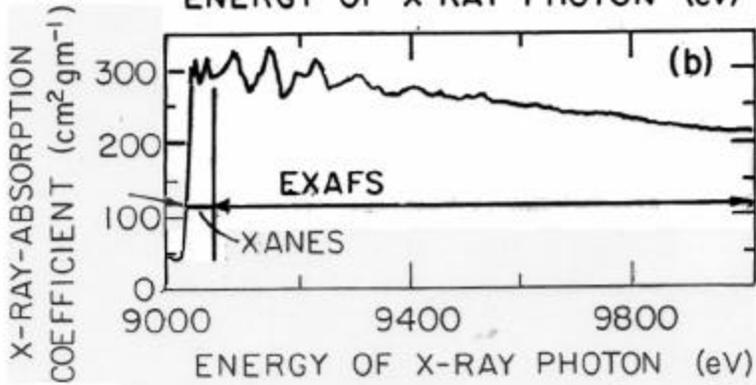
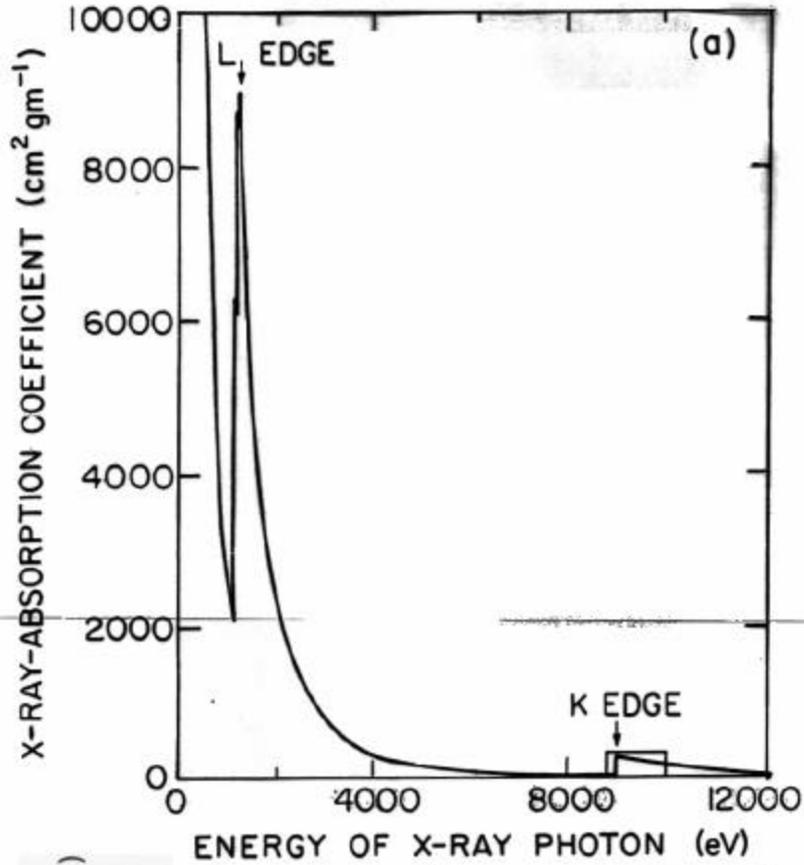
History of EXAFS

E. A. Stern

1. X-ray absorption edges discovered in 1912 and X-ray absorption Fine Structure (XAFS) Spectroscopy noticed in 1920's [Near Edge (XANES) 1920, Extended (EXAFS) 1929].

7) → (a)

Cu metal

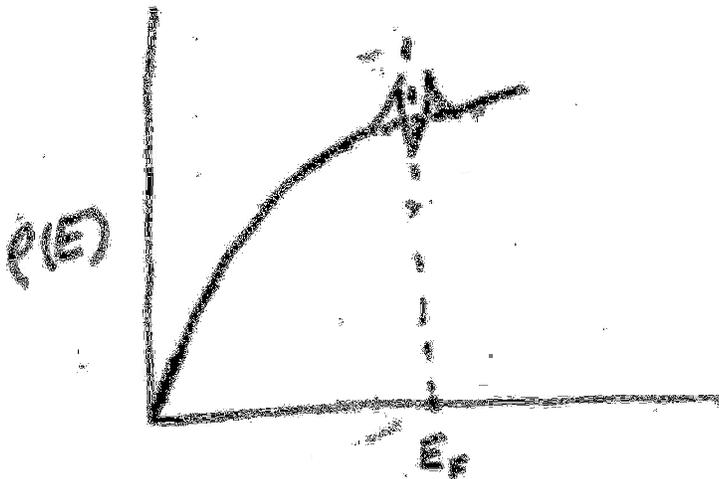
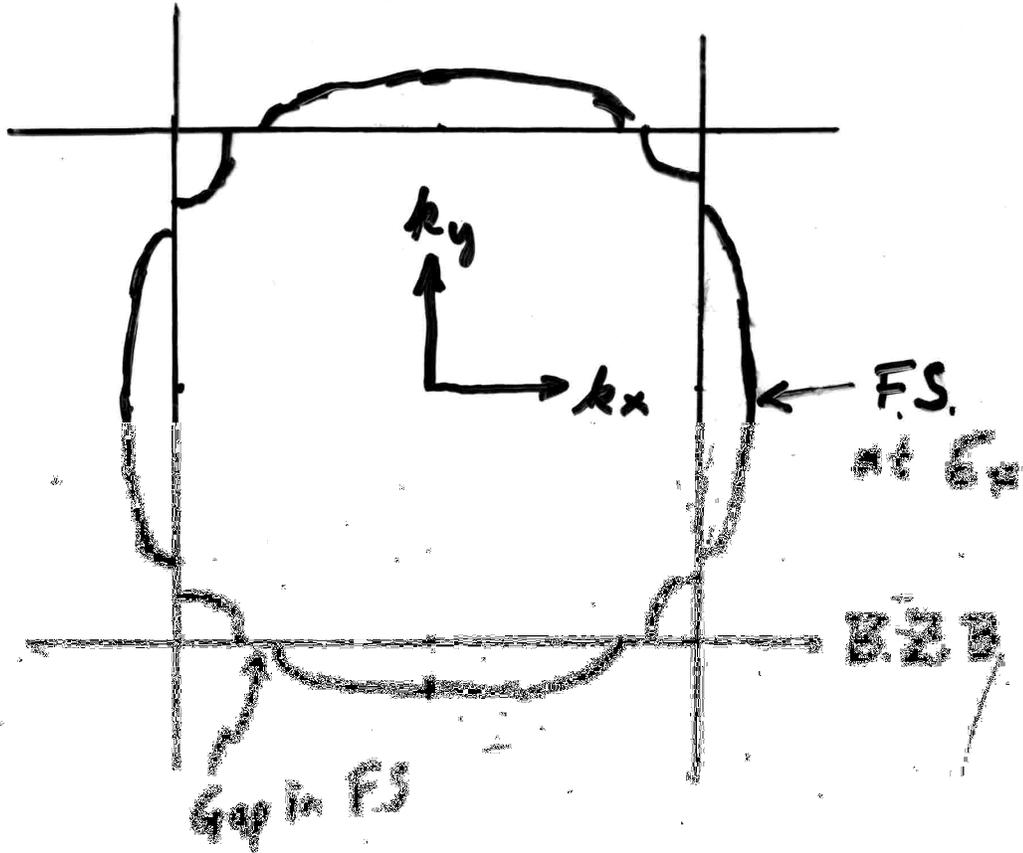


XAFS \equiv XANES + EXAFS

F L = 4 1 1

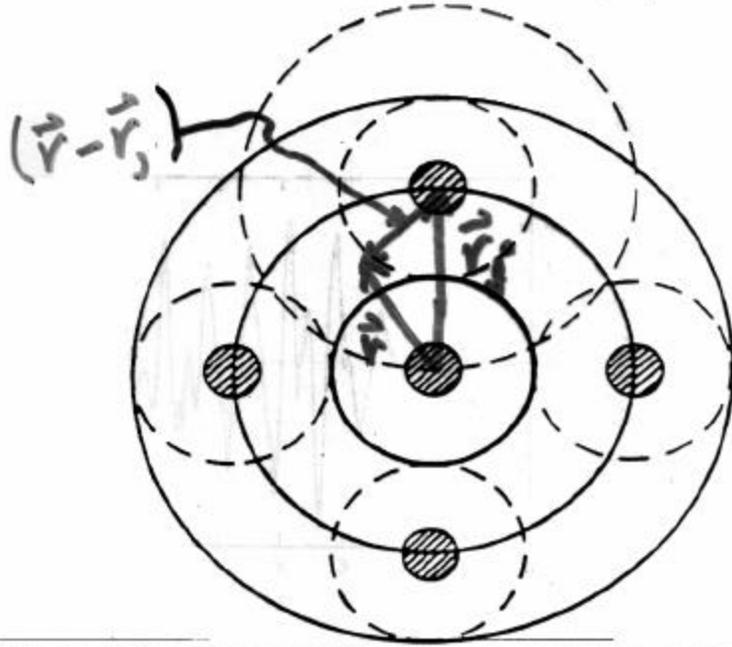
2. At that time spectroscopy was explained by electronic energy levels of Bohr. Near Edge fit Bohr, but not Extended.
3. Kronig in 1931, 1932 in 2 publications proposed EXAFS LRO theory based on electron energy bands and gaps in solids (Bloch).
Wrong!

Gaps in FS at BZB



4. After discovery that XAFS occurred in molecules Kronig in 1934 proposed a completely different theory, SRO theory, (related to modern theory except did not include Debye-Waller factor, mean free path and the correct phase shift. Also could not calculate the photoelectron-atom interaction correctly-no computers!)

8)

 $M \langle \psi_f | H' | \psi_i \rangle$ overlap only at origin


radial portion of photoelectron wave function. Multiplied by angular part depending on angular momentum

For dipole (Electric) transitions, the usual case for XAFS, and K-shell excitation ($1s, l=0$) the final state is a p-state ($l=1$) $\cos(\theta)$, θ is angle ^{from} between \vec{k}

5. EXAFS first called Kronig Structure.
6. Kronig never appreciated that SRO correct for both molecules and solids, and LRO theory wrong, causing confusion for 40 years. Disagreement between theory and experiment because *both* were wrong! Will now illustrate the experimental problems. Later in the Modern era section will discuss the error with the LRO theory of Kronig.

Extended Fine Structure in X-Ray Absorption Spectra of Certain Perovskites

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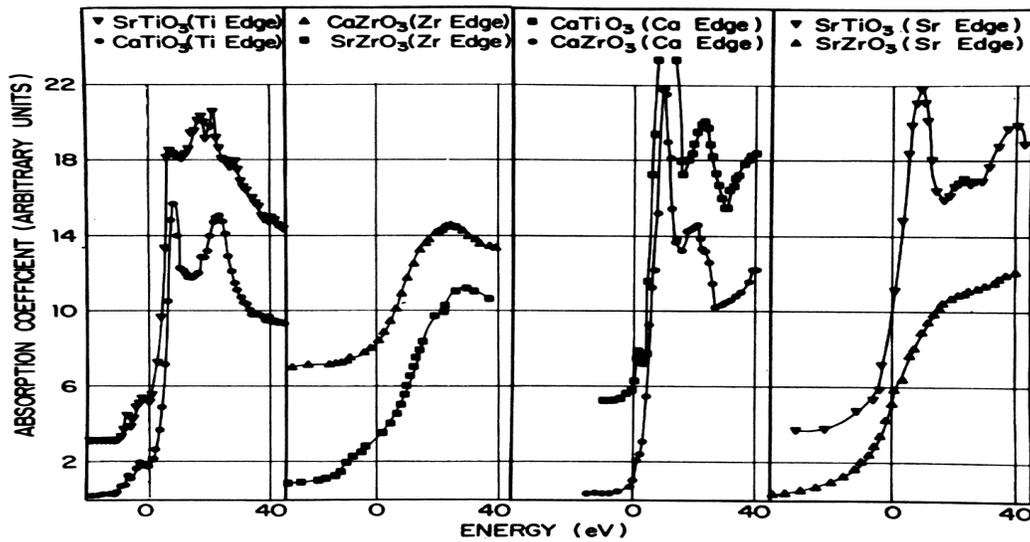
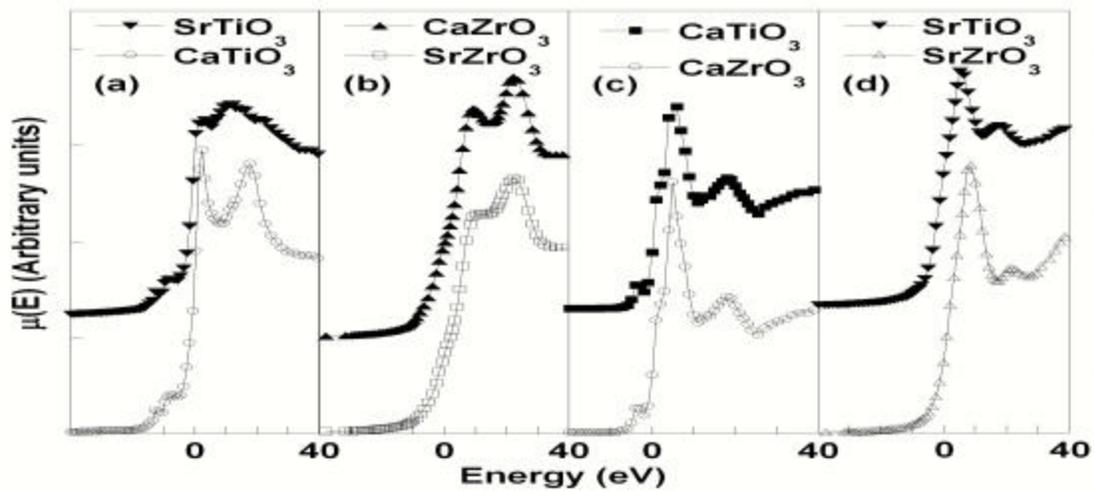
(Received 9 July 1969)

In this paper we attempt to test the validity of the short-range-order (SRO) and the long-range-order (LRO) theories of the extended fine structure (EFS) in x-ray absorption spectra. This is done by comparing the EFS's of Ti, Ca, Sr, and Ba in the perovskite-like compounds SrTiO₃, CaTiO₃, SrZrO₃, and CaZrO₃. The regularities which have been noted in these SRO or LRO theories have not been observed. We now have led to suggest that models are required other than those which have been used to explain the EFS.

I. INTRODUCTION

There is as yet no acceptable explanation of the extended fine structure (EFS) in x-ray absorption spectra. At present, two basically different theories attempt to explain this effect. The long-range-order (LRO) theory, introduced by Kronig,¹ attributes the EFS in crystals to the band structure of electronic energy levels. Qualitatively, this view correctly accounts for the relative displacements of the EFS extrema in crystallographically similar metals as well as for the similarity of EFS for the K edges of the components of certain binary compounds.²

The other point of view, the short-range-order (SRO) theory,³ is that the EFS arises primarily because the near neighbors of the absorbing atom influence the transition probability of the photoejected electron. Many features of the EFS which are believed to be capable of distinguishing between the two views are, on closer inspection, common to both. (For example, the dependence of the location of the characteristic absorption extrema on the inverse square of the dimensions of the cell is shared by SRO and LRO. Indeed this would follow even if the fine structure were due to recoil of the core electrons plus inelastic.) Qualitative successes for the SRO picture are found in the similarity of spectra in crystalline and amor-



Reference: E.A. Stern, "Musings about the Development of XAFS" *J. Synchrotron Rad.*, **8**, 49-54 (2001).

Modern

1. In 1965 Stern moves to UW, meets Farrel Lytle. Lytle has lab facility measuring EXAFS (before hard x-ray Synchrotron Radiation sources). Stern learns about EXAFS, has idea of modern theory in terms of the SRO theory, though, fortunately, he was not aware of the confused history of EXAFS.
2. Dale Sayers, first Stern grad student at UW, PhD thesis on EXAFS: develop theory with Stern and measure with Lytle.
3. Dale Sayers crucial role.

Dale had a crucial role, as excellent graduate students do, of performing most of the work on the initial theory and measurements, and developing the initial analysis software. Without his role there would not have been the continuity of effort to complete the transformation of EXAFS into its modern role as a local structure determination technique.

After Dale had worked out, under my supervision, the point scattering theory of EXAFS, which had essentially all of the physics of the modern theory (the hard part of the photoelectron-atomic interaction was set as parameters to be determined experimentally by comparing to

known structures), I posed to Dale the final part of his thesis – how to use the theory not to fit known structures, but to **determine unknown** structures. The success of this collaboration culminated in the publication of the 1971 PRL and the awarding of the PhD at the University of Washington to Dale in 1972.

[Sadly, Dale passed away last November at too early an age.]

4. 1971, PRL and FT: Ushering in the modern era of XAFS.

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray-Absorption Fine Structure*

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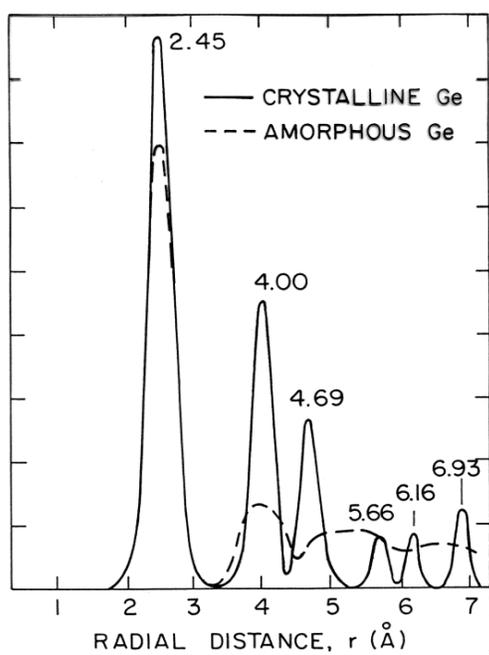
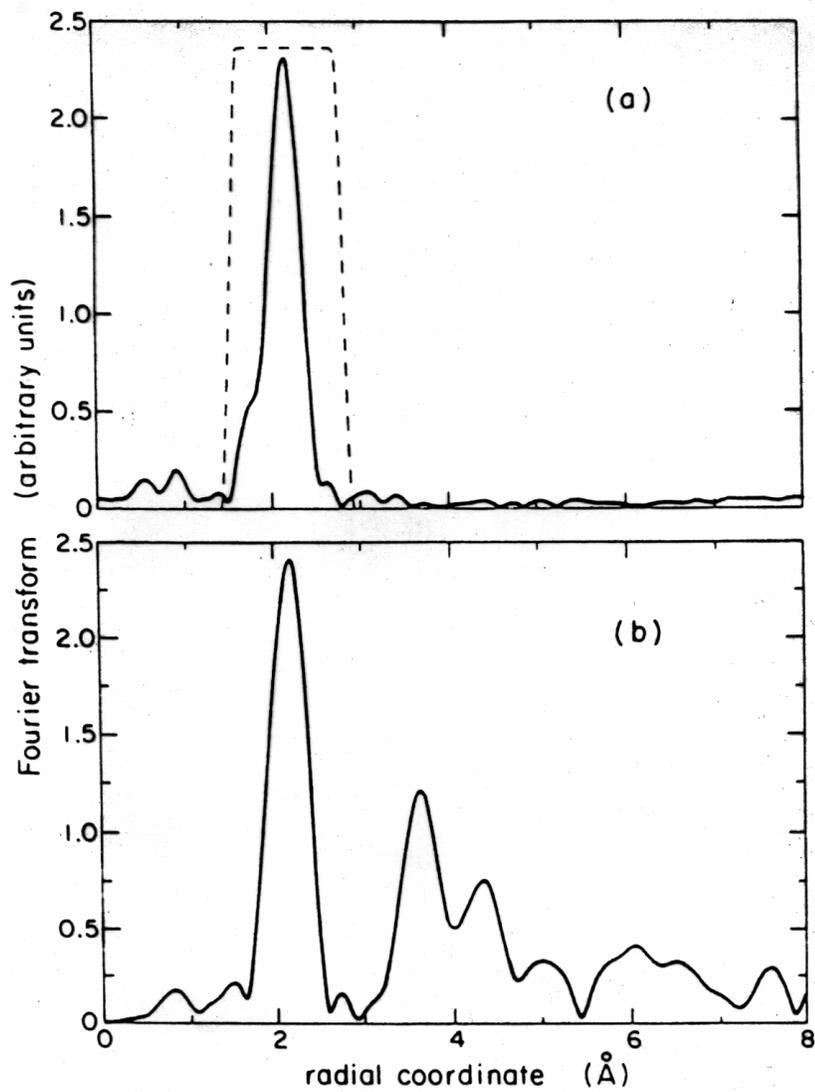
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(Received 18 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distances from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distances within the accuracy of measurement (1%).

Physicists have been tantalized for forty years¹ by the structurally sensitive extended x-ray absorption fine structure (EXAFS) or Kravig structure which appears on the high-energy absorption side of x-ray absorption edges. Recently, we reported a point-scattering theory of *K* x-ray absorption fine structure² which gave excellent agreement with experimental structure. In this Letter we show that the point-scattering theory can be used to invert formally the experimental EXAFS data to obtain a radial structure function containing interatomic distances, number of atoms, and widths of coordination shells in the absorbing material. Amorphous and crystalline Ge are compared to illustrate the technique.

EXAFS arises from oscillations in the photoelectric cross section due to scattering of the ejected photoelectron by atoms surrounding the absorbing atom. Our theory describes this surrounding atomic array in terms of a system of point scatterers. The total photoelectron wave function, including scattering, is calculated from scattering theory and used to calculate the dipole transition matrix element of which $\chi(b)$, the oscillatory part, is retained.² The final expression for the EXAFS is



The FT showed:

- SRO correct and circumvented the historic difficulty of proving which theory was correct.

- Way to **determine** structure by experimental standards (previously concentration on **understanding EXAFS**)

1. Atomic + structure parameters present

2. Can obtain atomic parameters by comparing with known structures' EXAFS

3. A series of three papers were then published which presented the details of how to use EXAFS as a **structure determination technique**. I. Theory [showed the mistake in Kronig LRO; gave standard and general form for

XAFS in SS]; II. Experiment [laboratory XAFS facility of Lytle]; III. Analysis [details of XAFS analysis and shows that the photoelectron-atom parameters are transferable between known structures and thus can be used to determine unknown ones for SS. Showed that MS effects were not present in first shell].

Theory of the extended x-ray absorption fine structure

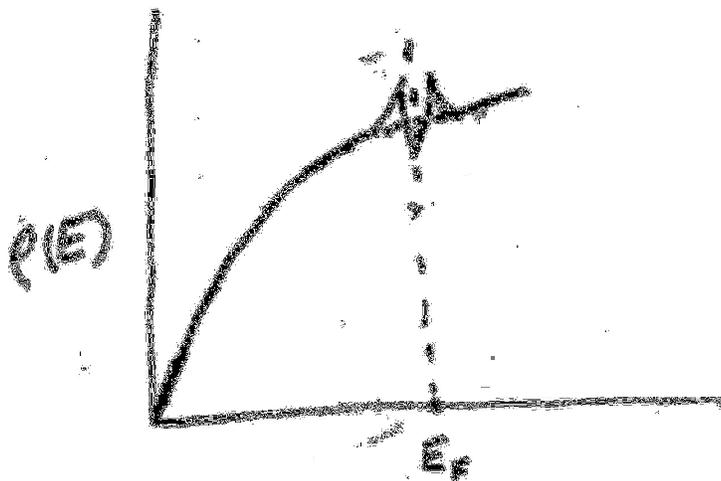
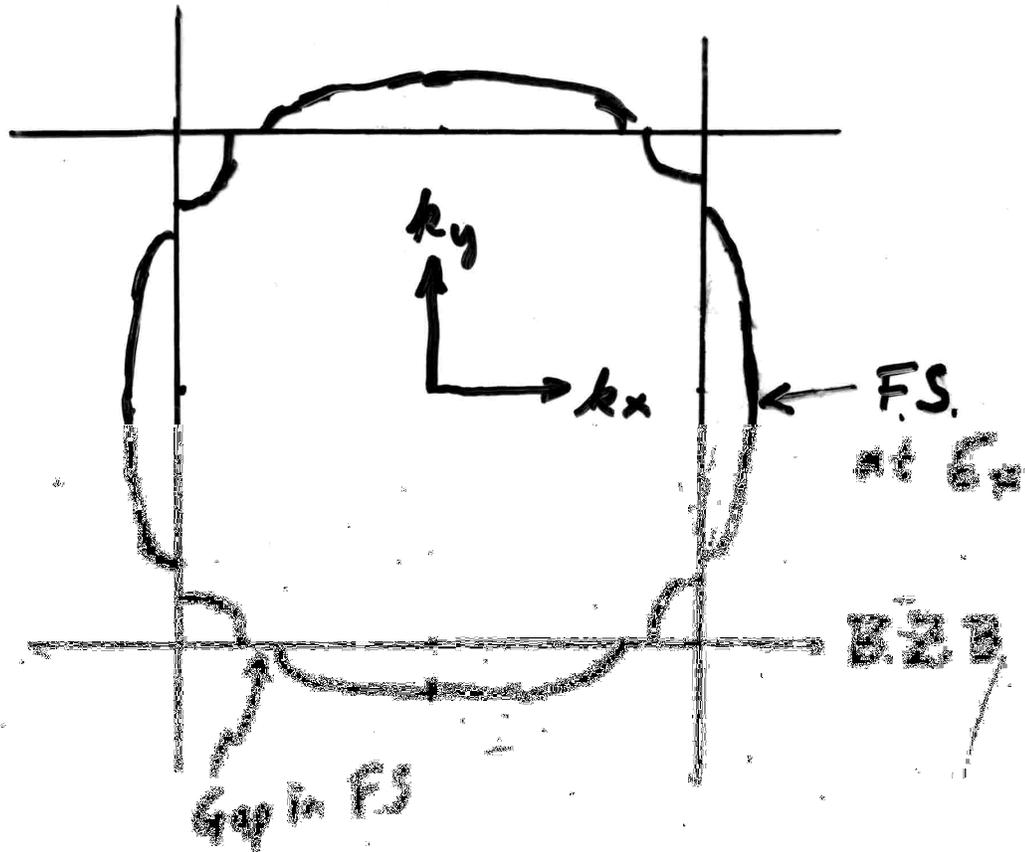
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(Received 14 March 1974)

A general theory of the fine structure observed on the high-energy side of the x-ray absorption edge (EXAFS) is presented. The form of the theory presented is used where the central atom is not too highly ionized and the potential is approximately spherically symmetric. A central concept is that of long-range-order theories of EXAFS and it is shown that the various oscillations are not the dominant mechanism as assumed previously. The oscillations are shown to be dominated by the scattering mechanism in the vicinity of the absorbing atom, and can most naturally be explained by a scattering mechanism in the immediate environment surrounding the absorbing atom. Under-standing the theory presented here requires an understanding of the spatial dependence of a scattering matrix. This scattering matrix is expressed in terms of the scattering of surrounding atoms, locating them, and can give information on the type of surrounding atoms and possibly the surrounding valence electron density. Because the theory is general, it can be used to obtain such information as can be obtained around each atom separately, making EXAFS a particularly powerful tool for determining the microscopic structure of condensed matter.

Gaps in FS at BZB



The structure introduced by the BZBs is just a rearrangement of electron states near the BZB which does not change the integrated number of states. In the EXAFS region the KE of photoelectron is much larger than the interaction energy with the solid and the gaps are of the order of 0.1 eV and less. The perturbation is integrated over by a much larger photoelectron lifetime broadening (>1 eV) erasing its effect. Thus the EXAFS is caused by the scattering of a decaying free electron photoelectron.

Extended x-ray-absorption fine-structure technique. II. Experimental practice and selected results

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(Received 23 December 1974)

A technique is presented for obtaining extended x-ray-absorption fine structure (EXAFS) using a conventional, high-resolution, x-ray fluorescence, Fourier transform spectrometer. Preparation of monochromator crystals, spectrometer alignment, scanning techniques, evaluation of the energy scale and data normalization techniques are discussed. EXAFS spectra from a wide variety of materials are then presented to show the variability of the effect and interplay between various parameters of the theory. A final section illustrates a simple graphical scheme to obtain a first-neighbors distance from EXAFS data.

1. INTRODUCTION

This, and the following paper¹ (referred to as III), describe the experimental details and data-processing techniques which have been developed for examination of the extended x-ray-absorption fine structure (EXAFS). Both papers are cast in terms of a recent general theoretical paper by Stern,² referred to as I. In this technique the

mediately surrounding the absorbing atom. It was shown that the EXAFS $\chi(k)$ can be accounted for by a scattering model⁷ formulated in I as

$$\chi(k) = \frac{m}{4\pi\hbar^2k} \sum_j \frac{N_j}{R_j^2} t_j(2k) e^{-2R_j/\lambda} \sin[2kR_j - 2k^2\sigma_j^2]$$

Extended x-ray-absorption fine-structure technique. III. Determination of physical parameters*

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(Received 23 December 1974)

Fourier transforms of extended x-ray-absorption fine structure (EXAFS) give structural information in the vicinity of each kind of atom, regardless of its wide variety of gaseous, liquid, and solid systems. A detailed description of the analysis of EXAFS data is presented including details of the Fourier transform of the data and the extraction of structural and other physical parameters from these transforms. Included in this description are the measurement of interatomic distances, coordination numbers, disorder effects (thermal and structural), energy-dependent electron scattering amplitudes, and phase shifts (phase shift and phase shift). EXAFS spectra of Ge, Cu, and GeO₂ are analyzed in detail. Multiple-scattering effects between atoms are generally found to be small. There are no multiple-scattering effects in the first shell of the Fourier transform. The phase shifts introduced by both the scattering and absorbing atoms are generally appear to be characteristic of the particular atoms and independent of the coordination for a given class of material. This is of great practical importance because it indicates that EXAFS may be calibrated by measuring known structures and then used to determine unknown ones.

4. Can then determine structure (single scattering)
- SS and MS. MS requires theory. John Rehr and FEFF (Josh Kas)
5. Several years later, Stanford Synchrotron Radiation Project (now SSRL), Dale helped build first XAFS beamline; opened up Modern era of XAFS to general scientific community.