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THE CHARACTERIZATION OF CRYOGENIC MATERIALS BY X-RAY ABSORPTION METHODS

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ABSTRACT

X-ray absorption techniques have in recent years been developed into powerful probes of the electronic and structural properties of materials difficult to study by other techniques. In particular, the extended x-ray absorption fine structure (EXAFS) technique can be applied to a variety of cryogenic materials. Three examples will be used to demonstrate the power of the technique. The first is the determination of the lattice location of dilute alloying additions such as Ta and Zr in Nb_3Sn . The Ta additions are shown to reside predominately in Nb lattice sites, while Zr is not uniquely located at either Nb or Sn sites. In addition to structural information, temperature dependent EXAFS studies can be used to determine the rms deviations of atomic bond lengths, providing information about the temperature dependence of interatomic force constants. For Nb_3Sn deviations are found from simple harmonic behavior at low temperatures which indicate a softening of the Nb-Sn bond strength. The final example is the study of interfacial properties in thin film systems. This is accomplished by making x-ray absorption measurements under conditions of total external reflection of the incident x-rays. As some examples will show this technique has great potential for studying interfacial reactions, a process used in the fabrication of many superconducting materials.

INTRODUCTION

Applications of Extended X-ray Absorption Fine Structure (EXAFS) measurements have expanded rapidly in recent years.¹⁻³ This has come about as a result of an improved understanding of the theoretical foundations of EXAFS and the availability of intense tunable x-rays from synchrotron radiation sources.⁴ As a result of these developments the EXAFS technique can be fruitfully applied to a number of cryogenic materials. In particular EXAFS measurements can provide local structural and dynamic information in a variety of systems including highly dilute or disordered systems for which traditional diffraction techniques have difficulties.

After a brief discussion of the origins of EXAFS, three different experiments are used to show the range of EXAFS measurements. The problems to be discussed are the site determination of dilute Ta additions to Nb_3Sn , a study of the temperature dependence of the

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interatomic forces in Nb_3Sn using the EXAFS Debye-Waller factor, and the use of total external reflection techniques to measure EXAFS of interfacial reactions.

BASIC PRINCIPLES OF EXAFS

EXAFS is the modulation in the x-ray absorption coefficient found above x-ray absorption edges for most materials. Figure 1a shows an example for the Nb K absorption edge in Nb_3Sn . The absorption increase or edge is a result of the opening up of a new channel for the x-ray absorption process. In the case of the K-edge it is the energy at which the 1s electrons can begin to be ejected. When this occurs the electrons are emitted as photoelectrons which can be described as an outgoing wave as shown in Fig. 2. This outgoing wave will scatter off the surrounding atoms resulting in interference. The interference can be

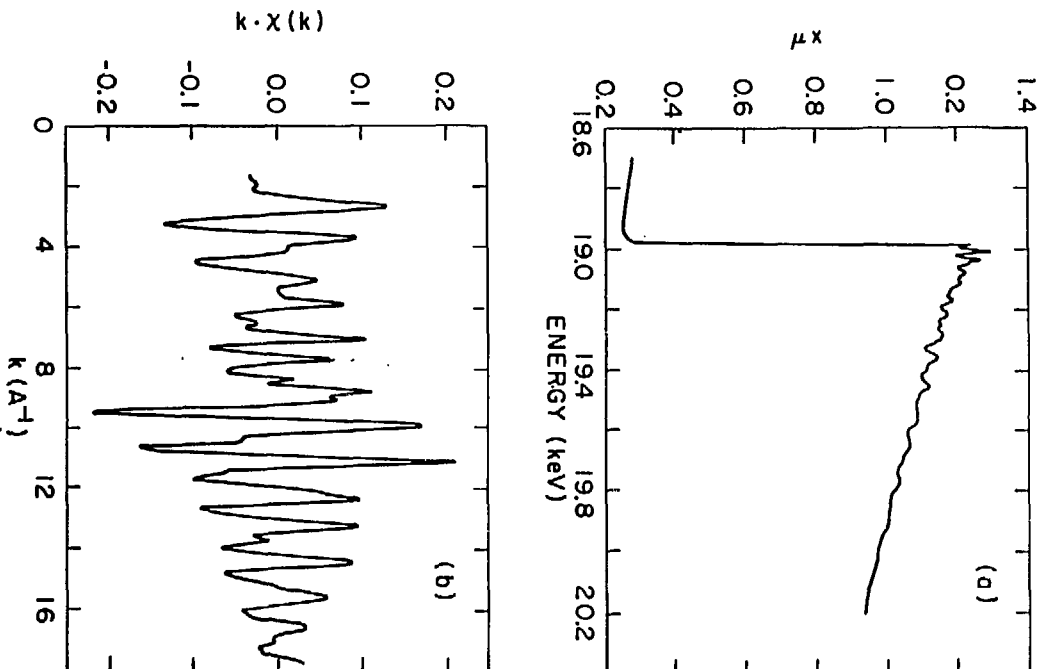


Fig. 1.

a) X-ray absorption at the Nb K edge in Nb_3Sn . b) The EXAFS oscillations, $\chi(k)$, in (a) multiplied by the wave vector k . The smoothly varying background absorption has been subtracted and the data normalized to the edge jump.

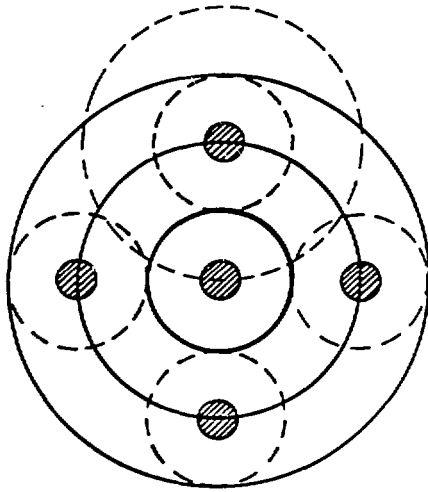


Fig. 2. Origin of the EXAFS oscillations. The spherical wave of the outgoing photoelectron scatters off the surrounding atoms. The interference between the outgoing and scattered waves modulates the X-ray absorption probability.

constructive or destructive depending on the relative phase of the outgoing and scattered waves. This gives rise to the oscillations in the absorption probability shown in Fig. 1. Thus, the EXAFS is a local probe providing information about the first few shells of surrounding atoms. In addition, since each element has its own distinctive absorption edge energy, the local environment of each component in a system can be probed by tuning the x-ray energy to the appropriate value.

For discussion purposes a simple independent particle model can be used. Putting the above qualitative discussion into mathematical form gives¹:

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

$$= \frac{m}{4\pi\hbar^2k} \sum_j \frac{N_j}{R_j^2} t_j(2k) \exp(-2R_j/\lambda) Q_j(k) \sin[2kR_j + \delta_j(k) + \phi_j(k)] \quad (1)$$

where k is the photoelectron wave vector, and μ_0 is the smoothly varying background absorption. The sum is over the neighboring coordination shells which contain N_j neighbors at distances R_j . λ is the mean free path of the photoelectron and the functions $Q_j(k)$ and $\phi_j(k)$ take account of any static or dynamic disorder in the j^{th} shell of atoms from their average distance R_j . The backscattering amplitude, denoted $t_j(2k)$, is a function of the type of backscattering atom, and $\delta_j(k)$ is the phase shift due to scattering from both the neighboring and central atoms. Typically $t(2k)$ and $\delta(k)$ are calibrated by measuring standard materials for which the structure is known.

As can be seen each shell of atoms contributes an oscillatory component to the EXAFS which has a frequency determined mainly by the interatomic distance, and an amplitude factor related to the types and number of atoms in a given shell along with any disorder present. Since each shell contributes a separate frequency, Fourier analysis is often used to analyze the data. Details of data analysis procedures are given elsewhere.^{1,2,5}

DILUTE CONSTITUENTS OF Nb₃Sn ALLOYS

A strength of the EXAFS technique is the ability to selectively study a dilute component in a system by tuning the energy to one of its absorption edges. From the local structural information obtained from the EXAFS it is often possible to locate a dilute constituent at a unique lattice position. The A15 lattice, which is common to a large class of superconductors including Nb₃Sn, is a good example. The local environments of Nb and Sn are quite different. Nb atoms have three nearby shells consisting of 2 Nb at 2.64 Å, 4 Sn at 2.96 Å and 8 Nb at 3.23 Å, while the Sn environment is much simpler with 12 Nb at 2.96 Å. These differences are easily seen in the data shown in Fig. 3. These are Fourier transforms of $\chi(k)$ data of the type shown in Fig. 1(b). As mentioned, each near neighbor distance gives rise to a distinct frequency which results in a peak in the transform. For the Nb data the three near neighbor distances give rise to a distinctive triple peak structure.

Alloying additions such as Ta or Zr are added to Nb₃Sn in an attempt to improve superconducting properties such as H_{c2} .^{6,7} Significant improvements in H_{c2} are found for Ta additions while adding Zr gives little

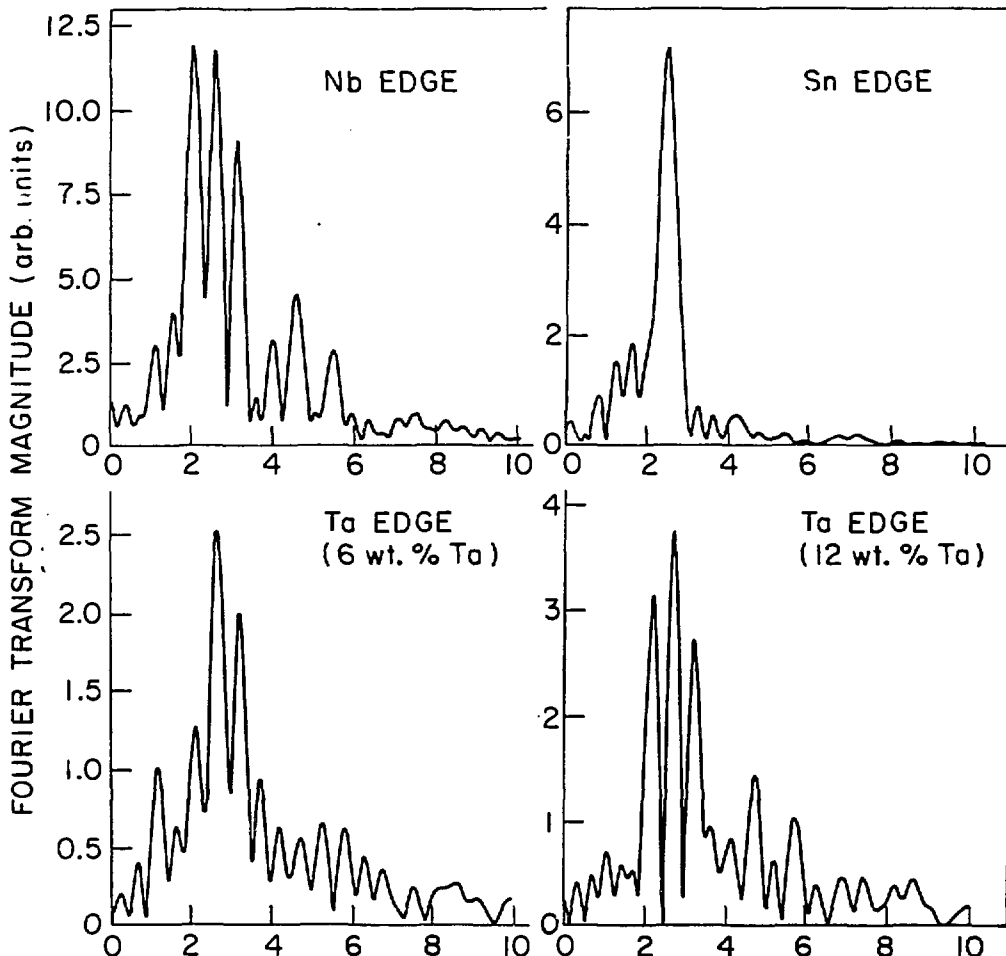


Fig. 3. Fourier transforms of $k \cdot \chi(k)$ for four cases. The Nb and Sn edges are for pure Nb₃Sn while the Ta edges are for Nb₃Sn samples which contain the indicated amounts of Ta.

change. Figure 3 shows transforms of EXAFS data taken for the Ta site in Ta-containing Nb₃Sn formed by the bronze process. It is clear from the similarities in the transforms that at higher concentrations the Ta atoms are sitting in Nb sites. This is in agreement with recent electron channeling results.⁸ The situation is not as clear for the lower concentration, but it still appears that most of the Ta atoms are on Nb sites. There is evidence from increased reaction rates of Ta-alloyed Nb₃Sn that some of the Ta resides in the grain boundaries.⁹ This would presumably involve a larger fraction of Ta atoms when the Ta concentration is low and could explain the observed differences.

For the EXAFS data obtained at the Zr edge the situation is different. The Zr transforms do not resemble either the Nb or Sn transforms. Further work is required to quantitatively determine the local Zr environment which will be the subject of a later publication.

INTERATOMIC FORCES IN Nb₃Sn

The parameters $Q(k)$ and $\Phi(k)$ take account of any disorder present in the bond length distribution of a particular coordination shell. The disorder can be due to static variations in bond lengths related to the inherent structure of the material, or a dynamic effect arising from the interatomic vibrations of the atoms and the fact that the x-rays take an instantaneous snapshot of the distribution. If there is no static disorder and a harmonic distribution is sufficient to describe the thermal vibrations then $\Phi(k) \sim 0$ and $Q(k) = \exp(-2k^2\sigma^2)$ where σ^2 is the mean square variation of bond length r . This EXAFS Debye-Waller factor is similar to the x-ray Debye-Waller factor except that it measures the variation in the bond lengths rather than deviations from the ideal lattice position. Therefore, the EXAFS σ^2 is a sensitive probe of interatomic force constants. Also, anharmonicity reveals itself by giving a nonzero $\Phi(k)$ and higher order terms in $Q(k)$.

The anomalous lattice dynamical behavior in high T_c Al₅ superconductors is well established. For Nb₃Sn, measurements of phonon dispersion,¹⁰ phonon density of states,¹¹ and elastic constants¹² all indicate significant softening of phonon modes as the temperature is lowered towards the Martensitic transition temperature ($T_M \sim 45$ K) where the cubic phase undergoes a small distortion resulting in a tetragonal structure. Questions remain concerning the connection between the phonon softening, the electronic structure, and the Martensitic phase transition. Some theoretical work¹³ has suggested that the Nb atoms see an anharmonic effective potential, and an x-ray diffraction study¹⁴ of V₃Si indicates that the V atoms vibrate anharmonically at low temperature.

EXAFS measurements of σ^2 for the Nb-Sn bond are shown in Fig. 4. Our results for the mean square fluctuations in the Nb-Sn nearest-neighbor distance indicate that as the temperature decreases, σ^2 decreases much less than would be expected from a harmonic Einstein model which fits most ordinary solids.¹ The extra contribution to σ^2 at low temperatures is most likely due to weakening of the effective Nb-Sn bond strength. Increasing static disorder could also explain the results, but there is no evidence for such disorder from other experiments. Anharmonic contributions to the EXAFS Debye-Waller factor are found to be negligible, so that at a given temperature the motion along the Nb-Sn bonds is harmonic. Further analysis should provide similar information about the motions of Nb-Nb pairs.

INTERFACE EXAFS

The index of refraction for x-rays is slightly less than one. If the incidence angle is small enough total external reflection can occur,

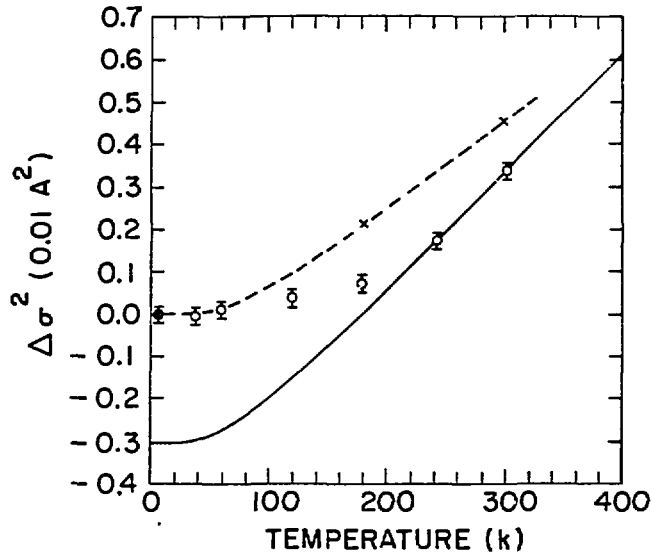


Fig. 4. Change in the EXAFS Debye-Waller parameter, σ^2 , as a function of temperature for the Sn edge in Nb_3Sn . The solid line is an Einstein model fit to the two highest temperature points and the deviation of the data indicates a softening of the Nb-Sn bond as the temperature is lowered. The x's are data for pure Nb which is fit well by an Einstein model (dashed line).

in which case the penetration of the x-rays into the surface is very small. For a material such as Cu the penetration is 20-30 Å. Similarly a reflection can be made to occur at the interface between an overlayer and substrate if the electron density of the substrate is larger. Again the penetration is only 20-30 Å, so that if a signal specific to the substrate is detected it will be due only to atoms located close to the interface. Thus, high sensitivity to interfacial regions can be obtained. One such element specific signal is the x-ray fluorescence excited by the incoming x-rays. The fluorescence intensity is directly proportional to the probability of absorption and, therefore, can be used to obtain the EXAFS spectrum.

An Al-Cu bilayer consisting of 1000 Å of Al on 1000 Å of Cu deposited on float glass was used to test the above ideas. For incident angles above the Al critical angle and below the Cu critical angle a strong reflection occurs from the interface. The EXAFS from the interfacial Cu atoms was then obtained by monitoring the Cu fluorescence as the incident x-ray energy was varied. The results are shown in Fig. 5 for various annealing temperatures. For temperatures below 140°C the spectra show the Cu to be in its normal metallic structure. At 160°C, however, an interfacial reaction forms a thin layer of CuAl_2 ,^{15,16} and the resulting spectra are a combination of those for Cu and CuAl_2 . At higher temperatures the CuAl_2 becomes thicker and the underlying Cu atoms are no longer reached by the reflecting x-rays; thus, the spectra show only CuAl_2 features.

Many materials, of which bronze process Nb_3Sn is a good example, are formed by solid state reactions. These glancing angle EXAFS techniques

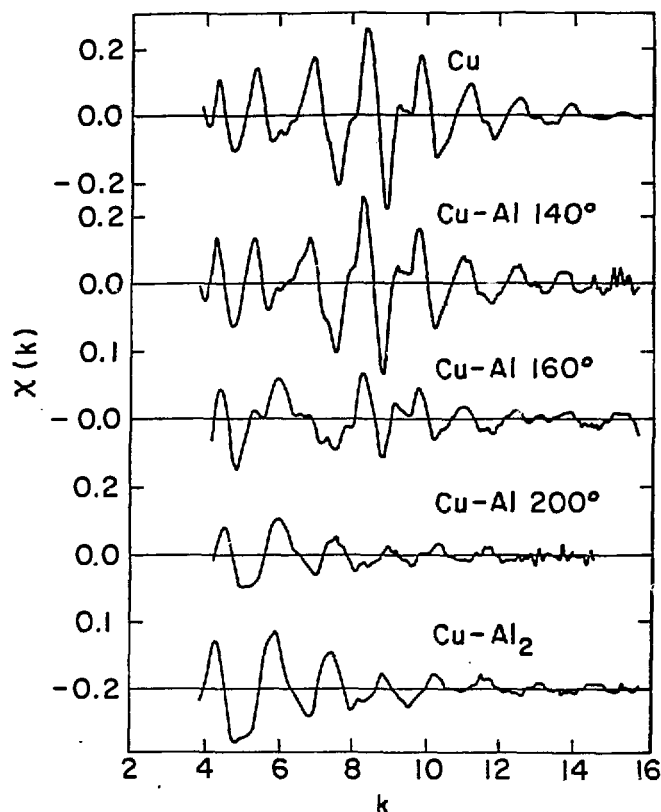


Fig. 5. EXAFS signal for a Cu-Al interface after annealing at 140, 160 and 200°C obtained using fluorescence detection and an incident angle of 4.5 mrad. For comparison, the spectra for pure Cu (top) and pure CuAl_2 (bottom) are also shown.

should find wide applications in the study of the microscopic structure of interfacial compounds. The high sensitivity to very thin interface regions make glancing angle EXAFS techniques especially sensitive to the initial stages of compound formation where nucleation problems are important.

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