

Local-Structure Determination at High Dilution: Internal Oxidation of 75-ppm Fe in Cu

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The local atomic environment around the iron site was measured in reduced and in oxidized dilute alloys of Fe in Cu. For these measurements a new detector was employed that extends applicability of the technique of extended x-ray-absorption fine structure to systems a hundredfold more highly dilute than those heretofore accessible. Details of the alloy study and implications for other research of the high sensitivity of this detector system are discussed.

Extended x-ray absorption fine structure (EXAFS) was first observed more than forty years ago,¹ but until the availability of the intense continuous radiation from electron synchrotrons EXAFS was not widely used for structural investigation. Even with this radiation source the method has not been applicable when the concentration of the species of interest in a host of roughly the same atomic number is less than about 1 at.%. In a system with a high- Z absorber in a low- Z host the limit is reduced roughly by the ratio of the absorption cross section of the host to that of the absorber. This would correspond, in a biological system, to a transition metal species at a concentration of about 0.01M. A new technique, by means of which the concentration limits are lowered by as much as a factor of 100, is described below. Dilute Fe in Cu has been studied with this technique and the results of the study are presented.

When an alloy containing very small amounts of Fe in Cu is annealed in oxygen, the low-temperature resistivity is found to be much less than that of hydrogen-reduced material.² For the 75-ppm Fe-Cu specimens used in this study the resistivity reduction factor is about 1800. This effect has been ascribed to clustering of the iron impurities during oxidation, which reduces the electron-impurity scattering.³ The experiments discussed here, designed to study local environments around the Fe atoms in reduced and oxidized states of this alloy, demonstrated that clustering indeed occurs upon oxidation, and provided the detailed structural information given below.

Variation of the absorption cross section of a species above a critical edge may be measured by effects on any of several quantities: transmission, fluorescence, Auger-electron yield, total electron yield. To attain the highest sensitivity for a minor constituent species in the bulk of a host material, x-ray fluorescence is generally best suited.⁴ Sensitivity limits at high dilution are set by signal-to-background ratios. With a specimen such as 75 ppm Fe in Cu this ratio would be extremely unfavorable; the fluorescence intensity is roughly only 10^{-4} times that of scattered radiation. Thus, for example, even with a photon-energy-sensitive semiconductor detector the Fe x-ray signal would be less than 1% of background.

With the technique described here, however, it is not difficult to achieve an improvement in signal-to-noise of about 10^4 and in dilution limit of about 10^2 . This improvement results from filtering the radiation from the sample before it reaches the detector with a focusing crystal analyzer designed to pass, in this case, only the Fe K x-ray fluorescence wavelength.

In Fig. 1, this analyzer, based on a Rowland circle geometry,⁵ is shown schematically. The crystals are installed on the inside of a barrel-like surface of revolution formed by rotating an arc of radius R_1 , equal to the focal Rowland-circle diameter, about the axis joining the sample (source) and detector. From the midpoint of the arc, the distance perpendicular to the sample-detector axis is $R_2 = R_1 \sin^2 \theta_B$, where θ_B is the Bragg angle for the fluorescent radiation. A

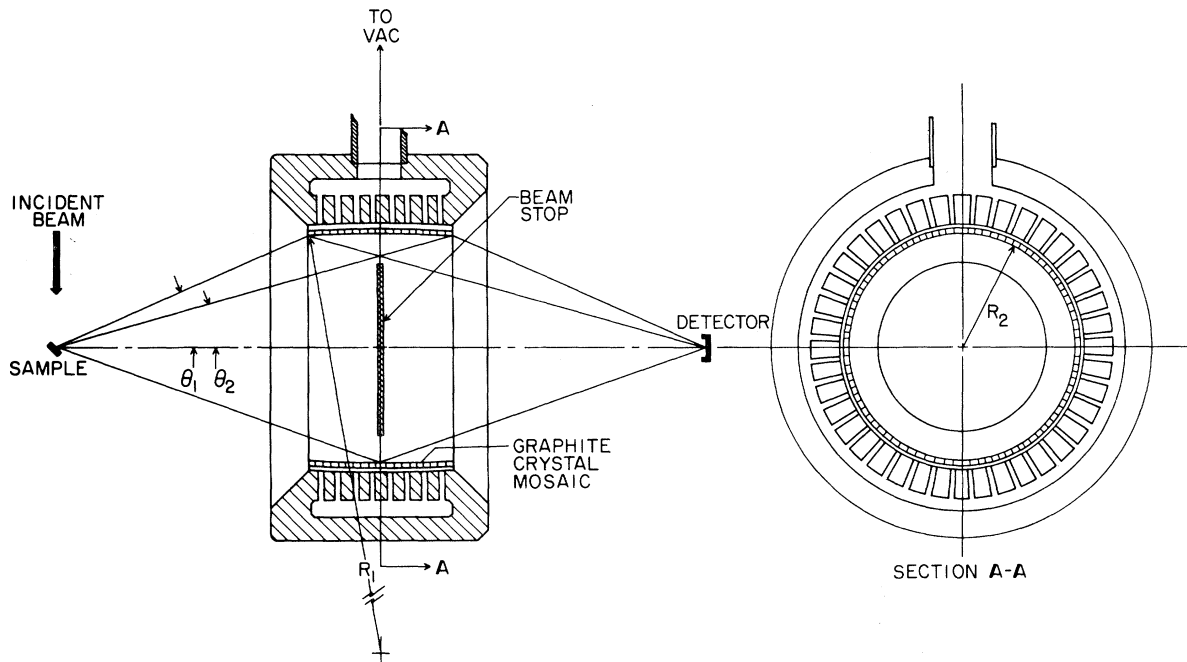


FIG. 1. Large-solid-angle crystal analyzer for filtering x-ray fluorescence from specimens in EXAFS measurements. Refer to text for definitions of radii and angles.

large solid angle of acceptance, Ω , given by Eq. (1) and in this case about 0.05π sr, is thus obtained. The solid angle is given by

$$\Omega = 2\pi(\cos\theta_1 - \cos\theta_2), \quad (1)$$

where θ_1 is the angle subtended at the source between the optic axis and the ray striking the nearest part of the crystal mosaic; θ_2 is the analogous angle for the ray striking the most distant part (cf. Fig. 1). Pyrolytic graphite was chosen for the crystals because of its high peak reflectivity and its mosaic spread, typically 0.5° which allows acceptance of $K\alpha$ radiation from the entire $\sim 0.01\text{-cm}^2$ sample area and rejection of the exciting radiation even at fluorescence threshold. The energy resolution required for this rejection in the case of K -shell fluorescence is not great; $\Delta E/E \sim 0.1$ is sufficient. Actual resolution of the analyzer is

$$\Delta E/E = \cot\theta_B \Delta\theta_B,$$

where

$$\Delta\theta_B = (\omega^2 + \varphi^2)^{1/2},$$

where ω is the mosaic spread and φ is an angle which takes into account the finite sizes of the source and crystal block and the source-to-crystal separation. In order that the filter-analyzer

may be used at any fluorescence wavelength, the barrel is exchangeable. A rough vacuum is applied to the outer side of the barrel and, because the wall is perforated, ambient pressure holds the graphite crystal assemblies in proper orientation against the inner surface. The "flexibility" required to make the graphite match the doubly curved surface is provided by making the crystals up as a mosaic of small blocks, $3 \times 3 \times 1 \text{ mm}^3$, glued onto a flat rubber backing sheet about 2 mm thick.

In the experiments described here, a small semiconductor detector, connected to a pulse amplifier and multichannel analyzer, was installed at the focus opposite the radiating source. Direct radiations from the source were prevented from entering this detector by a stop located midway along the source-detector axis. The filter-analyzer was employed in the study of local configuration about iron atoms in Cu-75-ppm Fe alloy.

The reduced specimen for these measurements was prepared by annealing the Cu-75-Fe alloy in H_2 at $\sim 1000^\circ\text{C}$ for one hour; the oxidized specimen was annealed in the same way but in air at 10^{-4} torr. EXAFS data were collected at the Stanford Synchrotron Radiation Laboratory with the storage ring operating with electrons only at nominally 3.5 GeV and 50 mA. The data were obtained

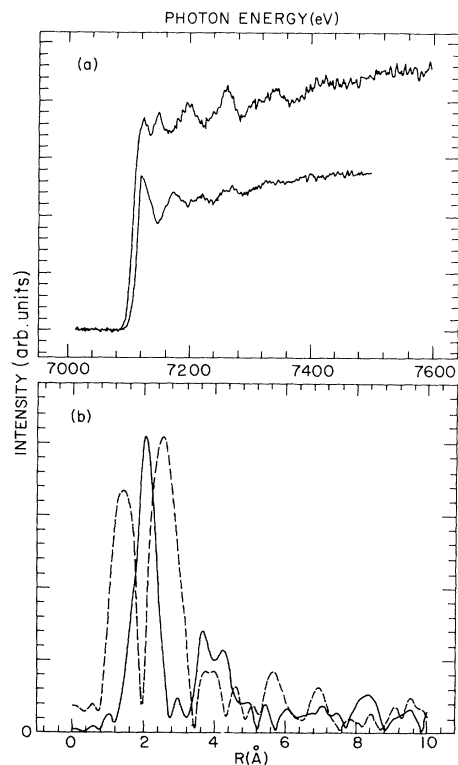


FIG. 2. (a) The observed EXAFS spectra from the oxidized alloy of 75 ppm Fe in Cu (lower curve) and hydrogen-reduced alloy of 75 ppm Fe in Cu (upper curve) after a linear background subtraction. (b) Fourier transforms of the net spectra after background subtraction, weighted by k (electron wave vector) but without phase-shift correction. The dashed curve is for the oxidized alloy and the solid curve for the reduced alloy.

at room temperature. The sum of several spectra, collected in a total of typically 200 min, after a linear background subtraction are shown, together with their Fourier transforms, for both the oxidized and reduced alloys in Fig. 2. Stan-

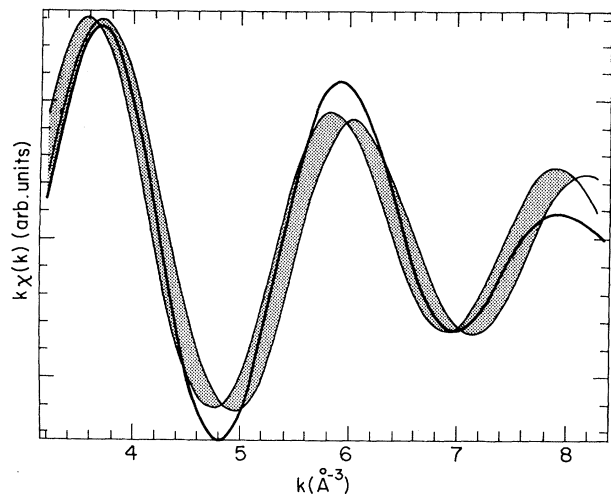


FIG. 3. Heavy curve: The back-transformed data from the first peak in the transform of the oxidized alloy. The shaded area covers the range of fits resulting from varying $R_{\text{Fe-O}} = 1.95 \text{ \AA} \pm 0.025 \text{ \AA}$.

dard analysis and fitting procedures^{6,7} were applied. In particular, after background removal, the spectra, weighted by k , are Fourier transformed into R space, shown in Fig. 2(b). The transforms are then multiplied by a smooth window function⁶ and back-transformed to k space,⁶ Fourier-filtering the data. The fitting is then done in k space, with use of the theoretical amplitudes and phase shifts of Teo and Lee⁸ and scale factors from model systems. The back-transformed data for the first peak in the transform of the oxidized alloy and a range of fits corresponding to $R_{\text{Fe-O}}$ of $1.95 \pm 0.025 \text{ \AA}$ are shown in Fig. 3. The data fall neatly between the two curves representing excursions of 0.025 \AA from 1.95 \AA for the iron-oxygen distance. The differences in amplitude between the fitted curves and the data are

TABLE I. Near-neighbor distances R , coordination numbers N , and Debye-Waller factors σ observed in EXAFS measurements for the atom pairs in the oxidized dilute alloy of 75 ppm Fe in Cu. For comparison, data are given for the equilibrium forms of Fe compounds which have been suggested (Ref. 3) as constituents of this material.

	$R_{\text{Fe-Fe}} (\text{\AA})$	$R_{\text{Fe-Cu}} (\text{\AA})$	$R_{\text{Fe-O}} (\text{\AA})$	$N_{\text{Fe-Fe}}$	$N_{\text{Fe-Cu}}$	$N_{\text{Fe-O}}$	$\sigma_{\text{Fe-Fe}} (\text{\AA}^2)$	$\sigma_{\text{Fe-Cu}} (\text{\AA}^2)$	$\sigma_{\text{Fe-O}} (\text{\AA}^2)$
75 ppm Fe in Cu, annealed in O ₂	3.09 ± 0.02	2.90 ± 0.02	1.95 ± 0.02	8 ± 2	4 ± 2	4 ± 2	0.06 ± 0.005	0.06 ± 0.005	0.05 ± 0.005
FeO	3.04		2.15	12		6			
Fe ₃ O ₄	2.96^a		1.81^a	6^a		4^a			
	3.47^b		2.09^b	12^b		6^b			
	3.62^c			4^c					
CuFe ₂ O ₄	2.96	3.47	2.09	6	12	6			

^{a,b,c}These superscripts designate corresponding coordination numbers and atom pairs.

due in part to electron mean-free-path effects. Effects of these differences on near-neighbor counts are small compared with the uncertainties quoted in Table I.

For the reduced alloy, the data yield the results 12 ± 2 near-neighbor Cu atoms at 2.54 ± 0.1 Å and a Debye-Waller factor 0.080 ± 0.005 Å. There was no indication of Fe near neighbors around Fe. The distance, very close to that in pure Cu, 2.556 Å, and the near-neighbor count together constitute independent indication that the iron atoms are isolated from each other in the Cu matrix. This is a condition consistent with the relatively high resistivity in the reduced state.

In published work,⁹ the steps proposed for the oxidation process are based on the partial pressures of oxygen required to form oxides from the pure metals. With increasing oxygen pressure, oxidation in the alloy should progress from Fe to FeO to Fe₃O₄ but not further to Fe₂O₃ because Cu₂O formation intervenes. Measurements of remanent moment and Curie temperature have led to the suggestion that copper ferrite, CuFe₂O₄, is the species produced in alloys containing 50 ppm or more of Fe³. EXAFS spectra obtained in these experiments for the oxidized alloy exhibit Fourier transforms, Fig. 2(b), having two distinct peaks and the contributions to each could be determined. Results are shown in Table I, where coordination numbers, near-neighbor distances, and Debye-Waller factors are given for Fe-Fe, Fe-Cu, and Fe-O atom pairs. Also tabulated are near-neighbor distances for FeO, Fe₃O₄, and CuFe₂O₄. Comparison of the sets of data shows that none of the equilibrium Fe compounds which have been proposed as constituents of the oxidized alloy can be identified in it, even though oxidation of the specimen, as judged by resistivity, was complete. Fe atoms appear to be clustered with Fe and have Cu and O near neighbors as well. The differences between interatomic distances seen in Fe-Cu alloy and those characteristic of the iron compounds must arise from the nature of the alloy environment in which the Fe clusters form; large local strains, for example, may exist.

In summary, a new EXAFS detection scheme has been tested in the study of internal oxidation of a dilute alloy of Fe in Cu host. A considerable extension of the limits of dilution to which the EXAFS method is applicable has been demonstrated. This new fluorescence filtering detector should be advantageous for studies of surface structure (SEXAFS)¹⁰ as well as for investigation of structure in dilute chemical and biological systems.¹¹

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