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EXAFS OF DILUTE SYSTEMS: FLUORESCENCE DETECTION**J. B. Hastings**

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Introduction

Since the first observations of the variation of the absorption coefficient for X-rays above the energy thresholds in the thirties until the early seventies, measurements and analysis of these variations were merely intended for the understanding of the underlying physics. Recently, with the understanding of the information available about the local atomic structure in the neighborhood of the absorbing species and the availability of high intensity synchrotron radiation sources, EXAFS has become a powerful structural tool. In the discussions that follow the details of the measurement for very dilute species will be presented. It is shown that for the more dilute systems the measurement of the emission rather than the direct absorption is a more favorable technique.

Fluorescence versus Transmission

The use of transmission EXAFS for concentrated systems is well established. When the systems under investigation become increasingly dilute in the absorbing atom there is a point where the signal to noise (S/N) ratio favors alternative techniques which measure signals characteristic of the absorbing species (x-ray fluorescence and Auger electron detection, for example). In the transmission mode, neglecting the statistics of the incident beam, the signal to noise ratio is given by¹

$$S/N = 0.735 \sqrt{I_0} \frac{\mu_x}{\mu_t} \quad (1)$$

where I_0 is the incident beam intensity and μ_x and μ_t are the absorption coefficient for the atom of interest and the total absorption coefficient of the sample, respectively. Both μ_x and μ_t are functions of the incident photon energy E and can be written as

$$\mu_x = N_x \sigma_x \quad (2)$$

and

$$\mu_t = \sum_i N_i \sigma_i \quad (3)$$

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where N is the density and σ is the absorption cross section, and the sum over i is for all atoms in the sample.

The signal to noise ratio for the case of fluorescence detection has to include the efficiency for detecting the characteristic X-rays from the atom of interest and the scattered intensity of the incident photon and may be written as

$$S/N = \frac{I_f \epsilon_f}{\sqrt{I_f \epsilon_f + I_s \epsilon_s}} \tag{4}$$

where ϵ_f and ϵ_s are the detection efficiencies for the fluorescent and scattered photons and I_f and I_s are the fluorescent and scattered intensities, respectively. I_f and I_s are given by

$$I_f = \frac{I_0 \omega_k f_k (\Omega/4\pi) \cdot \mu_x(E)}{\mu_t(E) + \mu_t(E_f)} \left\{ 1 - \exp \left[- \left(\mu_t(E) + \mu_t(E_f) \right) d \right] \right\} \tag{5}$$

and

$$I_s = \frac{I_0 \mu_t^*(E) (\Omega/4\pi)}{2\mu_t(E)} \left\{ 1 - \exp(-2\mu_t(E)d) \right\} \tag{6}$$

Here ω_k is the probability of producing a fluorescent photon of energy E_f after the creation of the appropriate core hole by an incident photon of energy E . f_k is the probability of filling the core hole with a given electron which produces a specific fluorescent photon energy. Both μ_t and μ_x , which have been defined previously, are explicitly written as functions of the incident energy E and the fluorescent photon energy E_f . $\mu_t^*(E)$ is the total scattering cross section for the sample including both the coherent and incoherent contributions. Finally, Ω is the solid angle subtended by the detector and d is the sample thickness. The angular dependence of the scattering cross sections due to the plane polarization of the incident beam has not been included.

By equating the signal to noise ratios for transmission and fluorescence for a given sample one can solve for N_x/N_t to get the concentration at which these two techniques are comparable. Assuming that the detection system cannot discriminate between fluorescent and scattered photons, $\epsilon_f = \epsilon_s$, and that the fluorescent intensity equals the scattered intensity, $I_s = I_f$, then

$$\frac{\mu_x}{\mu_t} = \left(\frac{1}{1.47} \right)^2 f_k \omega_k (\Omega/4\pi) \tag{7}$$

If further assume that $\sigma_x \sim \sigma_t$, $\omega_k \sim 0.5$ (ω_k for Cu is $\sim .5$), $f_k \sim 1$ and the detector subtends about 1% of the 4π sterad, we obtain

$$N_x/N_t \sim 2000 \text{ ppm.} \tag{8}$$

This qualitative estimate yields a lower limit for the concentration of the transmission technique. Is there a lower limit for the fluorescent technique? To answer this question, we shall assume that we have a perfect detector such that $\epsilon_f = 1$ and $\epsilon_s = 0$. Then the signal to noise is given by

$$S/N = \frac{I_f}{\sqrt{I_f}} \tag{9}$$

For a thick sample, $d \rightarrow \infty$, I_f is given by

$$I_f = \frac{I_0 N_x \sigma_k \omega_k f_k (\Omega/4\pi)}{\mu_t(E) + \mu_t(E_f)} \quad (10)$$

The variation of the product $\sigma_k \omega_k f_k$ as a function of the atomic number Z for K_α fluorescent radiation is shown in Figure 1.

To get an estimate for I_f we shall evaluate I_f at threshold energy where $E \sim 1.1E_f$ for the K edge. Assuming $\mu_t(E) \propto (1/E)^3$, we have

$$I_f \approx I_0 \frac{N_x}{N_t} \frac{\sigma_k \omega_k f_k}{\sigma_t} \cdot 0.43 \cdot (\Omega/4\pi) \quad (11)$$

For $(\Omega/4\pi) = 0.01$, $I_0 = 1 \times 10^{11}$ photons/sec which is typical of current storage ring synchrotron x-ray sources and an impurity concentration of $N_x/N_t = 100$ ppm, I_f for an Fe ($Z = 26$) or a Mo ($Z = 42$) impurity in various hosts is given in Table I. For an impurity with a Z comparable to that of the host, the total signal would be on the order of 10^4 to 10^5 counts/second. The EXAFS, however, represents somewhere between one and ten percent of the total signal. A one percent EXAFS therefore requires typically 10^6 counts/data point. It can easily be seen that the lower limits on concentration will always be source limited with a perfect detector and for the example shown may be of the order of 10 to 100 ppm of a low Z impurity in a high Z host.

For thick samples the ratio of the scattered to fluorescent intensities can be calculated from Eq. 5 and 6, as $d \rightarrow \infty$

$$\frac{I_s}{I_f} = \frac{\mu^*(E)/2\mu_t(E)}{\omega_k f_k \mu_x(E)/(\mu_t(E) + \mu_t(E_f))} \quad (12)$$

Assuming that no edges exist between E and E_f then $\mu_t(E_f) \approx (E/E_f)^3 \mu_t(E)$ and at threshold energy $E \sim 1.1 E_f$, we have

$$\frac{I_s}{I_f} \approx 1.2 \frac{N_t \sigma_t}{N_x \sigma_x f_k \omega_k} \quad (13)$$

With the value of $N_x/N_t = 1 \times 10^{-4}$ (100 ppm of the dilute specie) values of I_s/I_f have been calculated as a function of the atomic number of the host for several impurities. The results are shown in Figure 2. It is readily apparent that for all the impurities, I_s/I_f is typically 300 for hosts with atomic numbers similar to that of the impurity.

Detectors

At the heart of fluorescence EXAFS is the detection hardware. In this section three possibilities will be discussed: an integrating detector, a filter assembly² and a crystal analyzer,³ with emphasis on the crystal analyzer. Again, the signal to noise ratio for fluorescence EXAFS is

$$S/N = \frac{I_f \epsilon_f}{\sqrt{I_f \epsilon_f + I_s \epsilon_s}} \quad (14)$$

Factoring out $\sqrt{I_f}$ yields

$$1/\sqrt{I_f} \cdot S/N = \frac{\epsilon_f}{\sqrt{\epsilon_f + (I_s/I_f)\epsilon_s}} \quad (15)$$

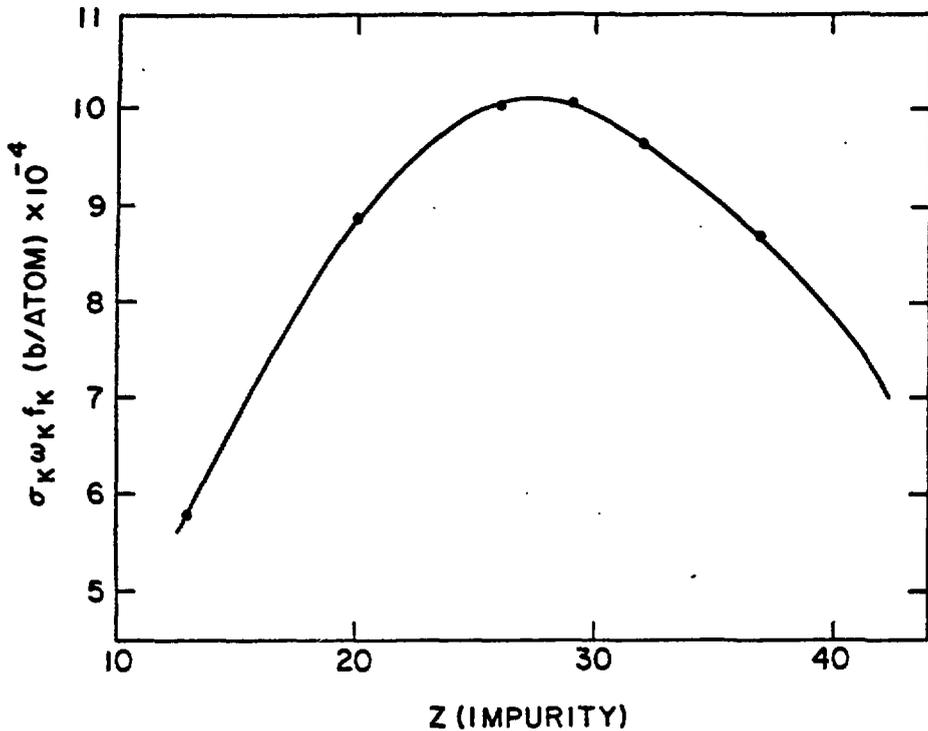


Fig. 1. Plot of the variation of the product of photoelectric cross section for the *K* hole, σ_k , radiative transition probability, ω_k , and the probability of filling the *K* holes with *L* electrons, f_k , as a function of the atomic number *Z* of the impurity.

Table I: Fluorescent Intensities I_f (counts/sec) for *Fe* or *Mo* Impurities in *C*, *Cu*, and *Nb* Hosts (assuming $\Omega/4\pi \approx 0.01$ and $I_0 \approx 1 \times 10^{11}$ photons/sec).

Impurity	Host	I_f
<i>Fe</i>	<i>C</i>	3.8×10^6
<i>Mo</i>	<i>C</i>	1.2×10^6
<i>Fe</i>	<i>Cu</i>	5.6×10^4
<i>Mo</i>	<i>Cu</i>	8.8×10^4
<i>Fe</i>	<i>Nb</i>	1.3×10^4
<i>Mo</i>	<i>Nb</i>	2.6×10^4

For fixed incident intensity, the three types of detectors can be compared using Eq. 15. Assuming the following detection efficiencies

- $\epsilon_f = \epsilon_s = 1$ integrating
- $\epsilon_f = 0.5, \epsilon_s = 0.05$ filter assembly
- $\epsilon_f = 0.1, \epsilon_s = 0$ crystal analyzer.

the values of $1/\sqrt{I_f} \cdot S/N$ can be calculated as a function of I_s/I_f for the three types of detectors using Eq. 15. The results are shown in Figure 3. It is apparent that the values of I_s/I_f for which the crystal analyzer is equivalent to the integrating detector and the filter assembly in terms of $1/\sqrt{I_f} \cdot S/N$ are 8 and 29, respectively. It should also be noted that the "normalized" signal-to-noise $1/\sqrt{I_f} \cdot S/N$ is independent of the solid angle. It is also emphasized that the crystal analyzer is advantageous for the most dilute systems, while the filter assembly is superior for the less dilute systems (N_x/N_t greater than 100 ppm).

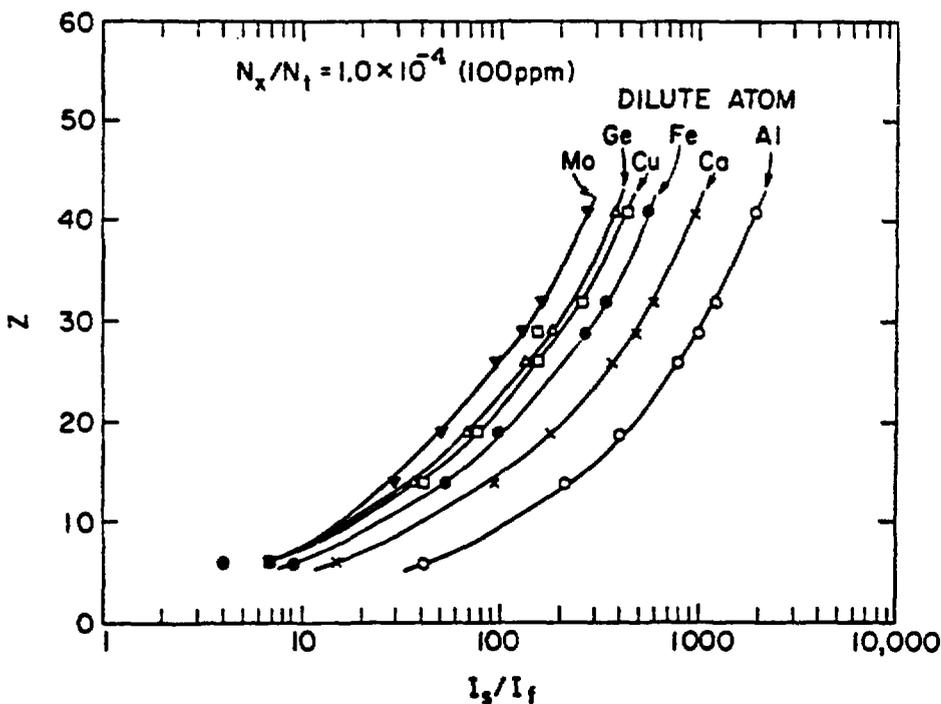


Fig. 2. Plots of the atomic number Z of the host as a function of the ratio of scattered to fluorescent intensities I_s/I_f for 100 ppm concentration of several impurities.

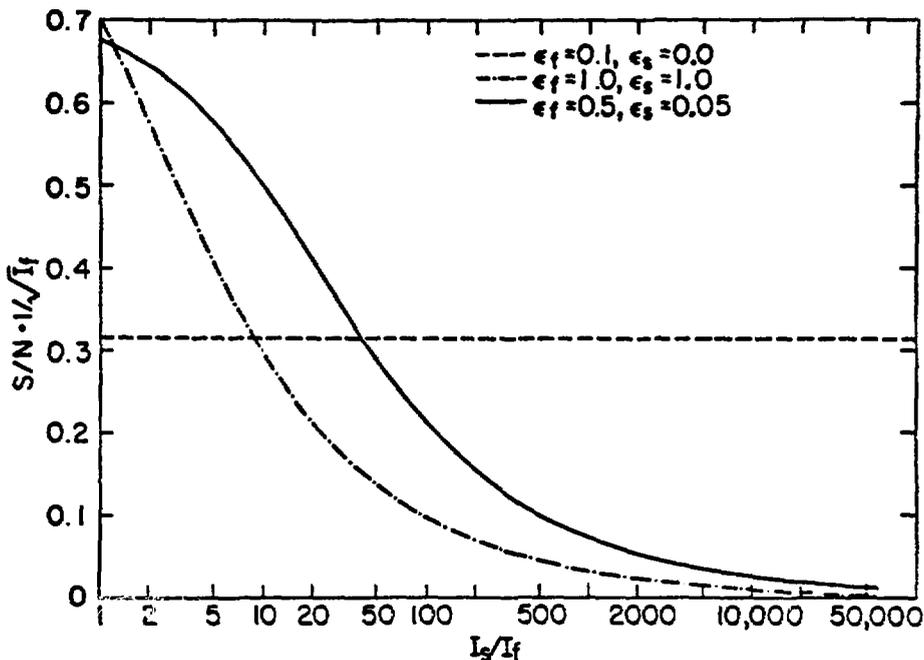


Fig. 3. Plots of the figure of merit $S/N \cdot 1/\sqrt{I_s/I_f}$ as a function of the scattered to fluorescent intensity ratio I_s/I_f for 3 choices of detector efficiencies corresponding to integrating detector, filter assembly and crystal analyzer (see text).

A crystal analyzer system has been constructed utilizing pyrolytic graphite crystals that can be held in a vacuum chuck to give a large solid angle and provide focusing to further improve signal to noise. The details of this scheme and its application to a study of internal oxidation of 75 ppm Fe in Cu are given elsewhere.³ A schematic diagram of this detector is shown in Figure 4.

Finally the variation of N_x/N_t for a given choice of impurity and host can be calculated with the formulas described in the previous sections. Assuming that the detectors subtend an equal solid angle, the crystal analyzer and filter assembly give an equal performance at $I_s/I_f = 29$. Figures 5 and 6 are plots of the variations of impurity concentration versus Z (atomic number) of the host for several impurities and Z of the impurities for several hosts, respectively, for $I_s/I_f = 29$. Both of these Figures show that except for high Z impurities in low Z hosts, the concentrations of impurity are greater than 100 ppm and in many cases as large as 1% for $I_s/I_f = 29$.

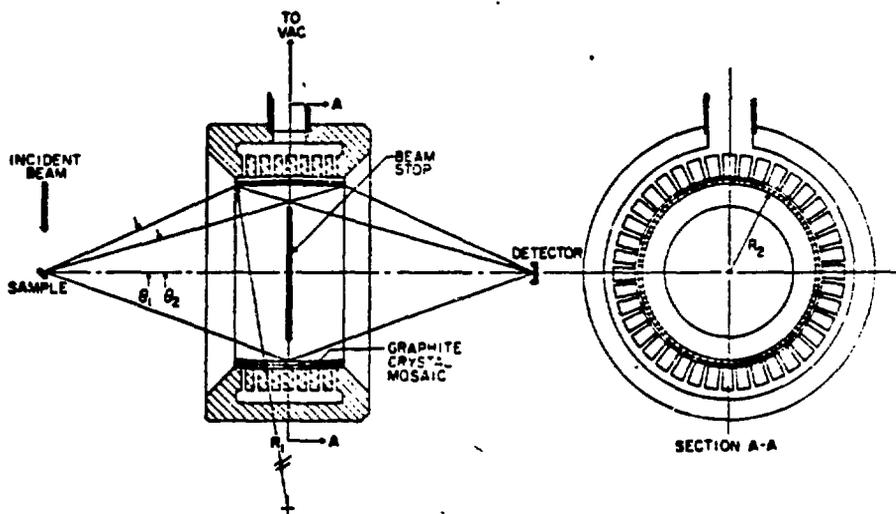


Fig. 4. Schematic diagram of a Rowland's Circle geometry crystal analyzer described in the text and in Ref. 3.

Summary

With the design and construction of dedicated storage rings, the development of EXAFS analysis, and advances in detection techniques, the investigations of the structure about dilute species are becoming more routine. With the aid of the calculations presented here the best techniques for the study of a specific system can be evaluated. In general for systems of biological interest where the Z of the dilute specie is large compared to the host the filter assembly is preferred. However, for metallurgical systems it may often be necessary to use a crystal analyzer.

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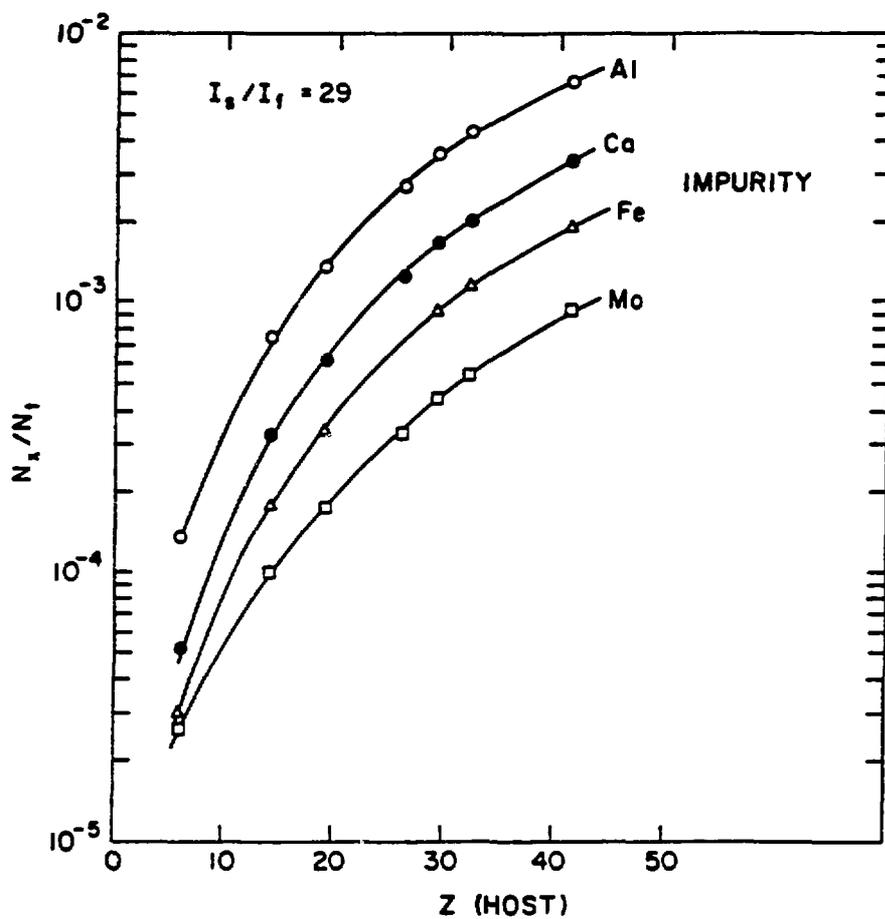


Fig. 5. Variations of concentration N_x/N_f of some dilute systems as a function of the atomic number Z of the host for several impurities. I_s/I_f is fixed at 29 (see text).

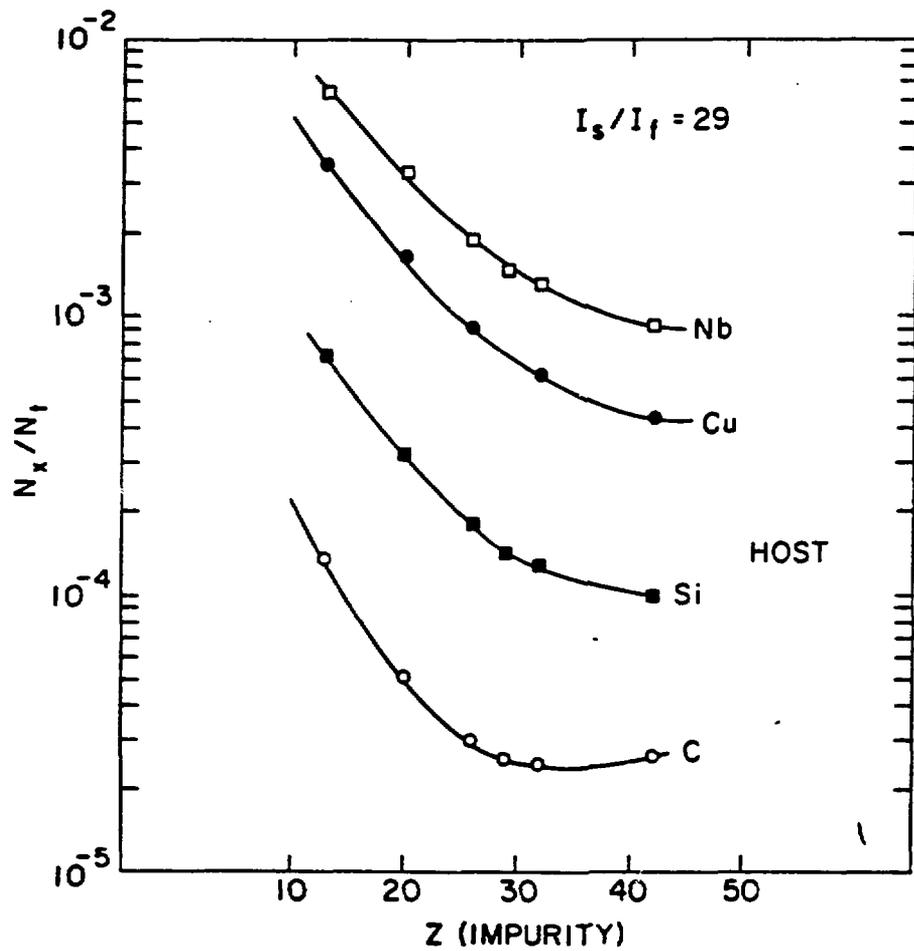


Fig. 6. Variations of concentration N_x/N_f of some dilute systems as a function of the atomic number Z of the impurity for several hosts. I_s/I_f is fixed at 29 (see text).

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