Separation of Different Atomic Shells in EXAFS Spectrum Using the Regularization Method

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Abstract.   It is shown that the regularization method with two kernels can resolve the double shells of different kinds of atomic species. The method was tested for simulated and experimental spectra. In both works, it provided successful results in separation of the double shells of different atoms.

1. Introduction

The extended X-ray absorption fine structure (EXAFS) technique has been used to examine the local structure of liquid and solid matters for several decades since the Fourier transformed skill was utilized in this field in 1971.[1] It has been applied to the analysis of the local structure of catalysis, amorphous and various functional materials. Recently, this technique has been used for various advanced materials containing many kinds of atomic species. However, it was very difficult to separate the double shells or the different atomic shells because it requires severe constraints among fit parameters. It has been shown that the regularization method provided higher R-space resolution for the double shell of monatomic materials,[2, 3], but there were still limitations on the separation of different atomic shells because of the difficulties of construction of the kernels for different atomic species. Nickel-titanium (so called nitinol) and related compounds are such materials. Nitinol is widely used for dental and medical applications because it exhibits an excellent shape memory effect.[4, 5]

Nitinol wire has a special nature with the super elastic and shape memory effect. It has the same atomic ratio of Ni and Ti elements, and the crystalline structure is monoclinic at the low temperature Martensite phase and cubic at the high temperature Austenite phase. The space group of the structure at the Martensite phase is $P_{21/m}$ and the cell parameters are $a = 2.898\mathring{A}$, $b = 4.108\mathring{A}$ and $c = 4.646\mathring{A}$ with the clinic angle $\beta = 97.78$. From the cell parameters, the atomic configuration was obtained by atomic bonds of $R_{Ni-Ti} = 2.53(3), 2.59(1), 2.60(3)$ and $3.28(1)\mathring{A}$ and $R_{Ni-Ni} = 2.61(2)$ and $2.90(2)\mathring{A}$ with the coordinates in parenthesis. It is very difficult to analyze the local structure with the conventional fit method for this material because mixed atomic shells with two different atomic species are included in its EXAFS spectrum.

In this work, we applied the regularization method with two kernels containing different atoms to the spectra of mixed shells to extract the shells in pair distribution functions. This was done by a simulation test and experiments.

2. Experiments

We performed EXAFS experiments for nitinol wire at 8C EXAFS beamline, Pohang light source (PLS), with the electron storage performance of 3.0 GeV and 300 mA electron beam current. The EXAFS experiments were conducted with the focused beam at Ni K-edge (Eo=7112eV). The proper fluorescence rejection filters were employed with the Mn filter. The solid-state detector (SSD) was installed at the detection site for the fluorescent measurements. The EXAFS data were analyzed by the conventional method using IFEFFIT [6, 7] and the regularization method.[2, 8, 9, 10]

3. Regularization method with two kernels of mixed shells

The EXAFS equation for multiple shells can be expressed by

$$\chi(k) = \sum_j \int \frac{N_j F_j(k, r_j)}{k r_j^2} e^{-\frac{2r_j}{\lambda(k)}} g_j(r_j)(\sin(2\mathrm{k}\mathrm{r_j} + \phi_\mathrm{j}(\mathrm{k}))\mathrm{dr_j} \tag{1}$$

where j and $g_j(r)$ indicate each atomic shell and distribution of the shell, respectively and N_j, $F_j(k, r_j)$, $\phi_j(k)$ represent the number of coordination, backscattering amplitude and phase of each neighboring scatterer, respectively.

The equation is transformed to matrix form as

$$\chi = Ag \tag{2}$$

where A is given by the matrix obtained from the EXAFS components in Eq.1. The element of matrix is calculated by the FEFF [11].

$$A = (A_1, A_2) \tag{3}$$

The g vector consists of two vectors, g_1 and g_2,

$$g = \begin{pmatrix} g_1 \\ g_2 \end{pmatrix} \tag{4}$$

where A is (n,n) matrix, and A_1, A_2 are (n, $\frac{n}{2}$) matrixes which are the kernels of shell 1 and 2, respectively, and g_1, g_2 are $\frac{n}{2}$ vectors which are the distribution functions of shell 1 and 2, respectively.

The pair distribution function of g_1 and g_2 can be obtained by the inverse procedure with regularization from Eq.2. The process of regularization in EXAFS analysis was described in detail elsewhere [3, 8]

4. Analysis of Simulated Spectrum

EXAFS spectra shown in Figure 1-(a) for Ni-Ti (green dash line), Ni-Ni (red dot line) and Ni-(Ti,Ni) (black line) shells have been calculated by FEFF with the pair distribution functions (indicated by "model") shown in Figure 1-(b) and (c), and the two spectra were merged to make a double shell spectrum of different atomic species. Each EXAFS spectrum and the related equations were prepared as a vector or a matrix form for the regularization procedure. Here, A was (200 × 200) matrix, and A_1 and A_2 was (200 × 100) matrices.

The pair distribution functions of Ni-Ti and Ni-Ni pairs extracted from the simulated EXAFS spectra are shown in Figure 1-(b) and (c). As shown in 1-(b), the pair distribution function (green dash line) extracted from the Ni-Ti single shell spectrum almost fits the model (black line) as expected. The pair distribution function (red dot line) obtained from the merged spectrum deviated slightly from the model one but fits fairly. As shown in Figure 1-(c), the pair distribution functions of Ni-Ni shells also fit well to the model one within an acceptable error
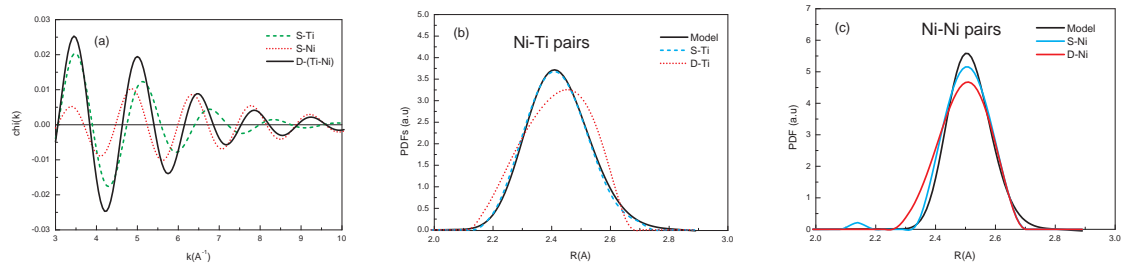
Figure 1. Comparison of simulated EXAFS spectra, and the modeled and reconstructed pair distribution functions. (a) EXAFS spectra for Ti shell only (green dash line), Ni shell only (red dot line), mixed shells (black line). (b) The pair distribution functions of Ni-Ti pairs for Model (black line), extracted from Ti single shell (green dash line), extracted from mixed shells (red dot line), (c) The pair distribution function of Ni-Ni pair for model (black line), extracted from Ni single shell (green line), extracted from mixed shells (red line).
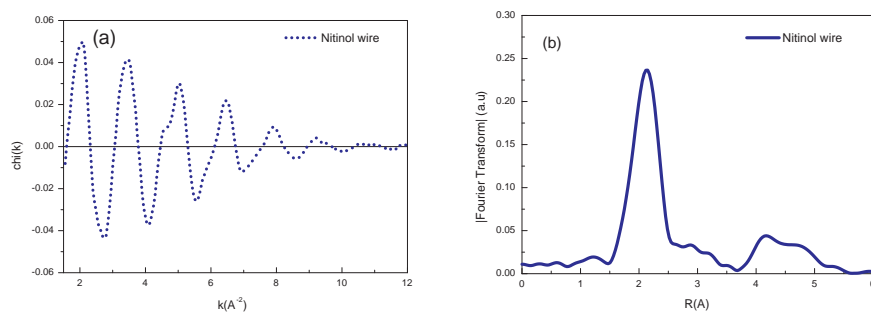

Figure 2. (a) Experimental EXAFS spectrum of nitinol wire and (b) its Fourier transform.

margin. From this simulation test, we see that the pair distribution functions of different kinds of atomic shells can be obtained separately from the merge spectrum without any constraint.

5. Analysis of Experimental Spectrum

Nitinol is very suitable to test the separation of double shells of different atomic species. Figure 2-(a) and (b) show the experimental chi(k) spectrum and the Fourier transformed spectra obtained by experiment for nitinol wire.

As shown in Figure 2-(a) and (b), the EXAFS spectrum of nitinol wire looks almost like single shell features. However, we know that the atomic arrangement around Ni central atoms in nitinol consists of multiple shells of different atomic species. The experimental EXAFS spectrum shown in Fig. 2-(a) was analyzed by the regularization method to extract the pair distribution functions. The main peak in Figure 2-(b) within the window $R = (1.73 - 2.65)\mathring{A}$ was filtered by the inverse Fourier transform to extract chi(q) spectrum to be processed by the regularization method.

Fig. 3-(a) and (b) show the obtained pair distributions of Ni-Ti and Ni-Ni shells, respectively, and Fig. 3-(c) shows the fit of the filtered spectrum to the calculated spectrum by the regularization method. The peak at $R = 2.51\mathring{A}$ in Fig. 3-(a) corresponds to the Ni-Ti bond at $R = 2.53\mathring{A}$ in the crystallographic data. Also, the peak at $R = 2.96\mathring{A}$ in Fig. 3-(b) corresponds to the Ni-Ni bond at $R = 2.90\mathring{A}$ in the crystallographic data. The other peaks near $R = 3.25\mathring{A}$
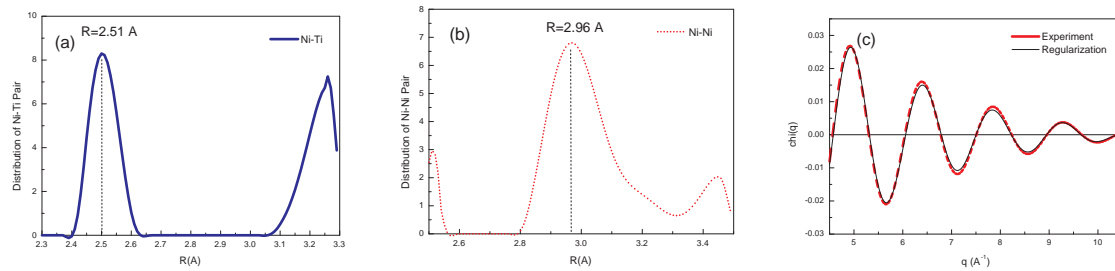
Figure 3. Pair distribution functions obtained by regularization method for Ni-Ti (a) and Ni-Ni (b), and EXAFS spectra (c) filtered from the experimental spectrum (red dash) by inverse Fourier transform and calculated (black solid line) with the pair distribution functions obtained by the regularization method.

and $R = 3.43\mathring{A}$ are related to other bond lengths.

Fig. 3-(c) shows the chi(q) spectra obtained by the experiment (red dash) and calculated with the pair distribution functions. As shown in Fig. 3-(c), the reconstructed spectrum fits accordingly to the experimental one. This means that the pair distributions and the bond length were estimated properly with the regularization method.

As pointed out, it was very difficult to separate the merged shells of different kinds of atomic shells with the conventional fitting technique because the two shell fitting requires many fit parameters exceeding the limitation of fit variables. However, as shown in Fig.3, the regularization method provided an adequate separation of pair distribution functions of merged shells of the two different kinds of atoms, but the bond length was not matched exactly to the crystallographic data. This means that this method needs more sophisticated skills to provide clearer structural information of the mixed shells of different atomic species.

6. Summary

In this work, we showed that the regularization method with two kernels can resolve the merged shells of two different kinds of atoms. It was tested by simulation and experimental works. In both works, the regularization method with two kernels provided successful results in separation of the double shells.

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