

Comment on "Simple Method for the Evaluation of Bond Length from Data"

Recently Mahto and Chetal¹ claimed that they can obtain extended x-ray-absorption fine-structure (EXAFS) nearest-neighbor distances that agree closely with crystallographic data by fitting the total phase to an expression of the form $2kR + \delta(k)$ with $\delta(k) = c_0 + c_1 \times \exp(-c_2k)$. The exponential is included to cause $\delta(k)$ to vanish for large k . E_0 , the origin of the k scale, is not a parameter here but c_0 nearly compensates for a variation of E_0 . We have tried their model on crystalline Ge. Least-squares fitting of the phase in the range from 6 to $13 \text{ \AA}^{-1}$ resulted in $R = 2.19 \pm 0.03 \text{ \AA}$ which differs from the crystallographic value of $2.45 \text{ \AA}$ by 11%. Figure 1 shows the residual sum of squares, Σ^2 , as a function of R where a fit was performed for fixed values of R . The uncertainty of R is defined by the region where $\Sigma_{\min}^2 < \Sigma^2 < 2\Sigma_{\min}^2$. For comparison we have included the result of a fit using phases published by Teo and Lee² where E_0 is the only parameter, with the result $R(\text{Ge-Ge}) = 2.434 \pm 0.01 \text{ \AA}$. The correct crystallographic distance, $2.45 \text{ \AA}$, is indicated by the arrows.

We then tried to reproduce some of Mahto and Chetal's results but failed. For one Cu spectrum ($4 < k < 13 \text{ \AA}^{-1}$) no minimum of Σ^2 could be found at all. The parameters were strongly correlated because the value of c_2 was such that $c_2k < 1$ so that the exponential was nearly a straight line. Another Cu spectrum ($4 < k < 15 \text{ \AA}^{-1}$) did produce a minimum (Fig. 1) but at $R(\text{Cu-Cu}) = 2.26 \pm 0.03 \text{ \AA}$. The fitting of both Cu spectra over the respective ranges with use of Teo and Lee's theoretical phase gave $R(\text{Cu-Cu}) = 2.51 \pm 0.01 \text{ \AA}$. This is a little smaller than the accepted value $2.56 \text{ \AA}$ and points out the merit of the use of a reference compound to determine the phase. In addition, we tried to use Mahto and Chetal's method to fit Ni-metal and NiO spectra from 6 to $14.5 \text{ \AA}^{-1}$ and obtained $R(\text{Ni-Ni}) = 2.21 \pm 0.04 \text{ \AA}$ and $R(\text{Ni-O}) = 1.9 \pm 0.1 \text{ \AA}$, respectively. The crystallographic values are 2.492 and $2.08 \text{ \AA}$.

The phase cannot be obtained from the EXAFS of a single shell by the determination of the positions of the maxima and minima as mentioned in their Eq. (7) because the amplitude is not constant. The phase can be determined independently of amplitude by the zero crossings or, preferably, by use of the Fourier-transform method.³ The phase does not depend on the weighting employed in the k -to- R transform as implied by Mahto

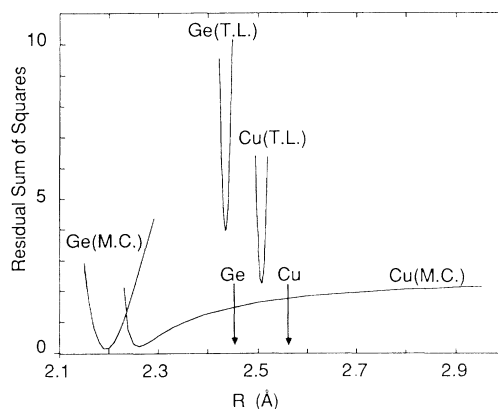


FIG. 1. Residual sum of squares for fits to Cu and Ge EXAFS spectra by use of Mahto and Chetal's (M.C.) model and by use of Teo and Lee's (T.L.) theoretical phases allowing E_0 to vary. The arrows indicate crystallographic distances of Ge and Cu.

and Chetal's statement that a k'' weighting in the Fourier transform "prevents the need of any correction in E_0 at higher k values."

For $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ Mahto and Chetal do not list the crystallographic value for the nearest-neighbor distance but obtain $R = 2.00 \text{ \AA}$. According to Ref. 4 the first-shell Cu-O distance has a mean value of $2.18 \text{ \AA}$.

It seems then that the model of Mahto and Chetal is not a reliable way of obtaining nearest-neighbor distances.

K. R. Bauchspiess, N. Alberding, and E. D. Crozier
Department of Physics
Simon Fraser University
Burnaby, British Columbia, Canada

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