

Note on the K extended X-ray absorption fine-structure Debye-Waller factor

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 8029

(<http://iopscience.iop.org/0953-8984/4/40/015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:39

Please note that [terms and conditions apply](#).

Note on the K extended x-ray absorption fine-structure Debye–Waller factor

Tadao Ishii

Faculty of Engineering, Okayama University, Okayama 700, Japan

Received 10 February 1992, in final form 12 June 1992

Abstract. The cumulant expansion of the EXAFS Debye–Waller factor is discussed for the polarized and ‘non-polarized’ K EXAFS formulae. The improved formula for the non-polarized EXAFS turns out to give a shorter near-neighbour distance than the value obtained by the expansion derived previously. Specifically, in CuBr at around 600 K its difference is about 0.01 Å.

1. Introduction

The basic formula of polarized K extended x-ray absorption fine structure (EXAFS) is given in the plane-wave approximation under the condition $kR_{AB} \gg 1$ in the form [1–4]

$$\chi(k) = -\text{Im} \left[(\epsilon \cdot \hat{R}_{AB})^2 \sum_B \frac{3}{kR_{AB}^2} f_B(k, \pi) \times \exp[i2(kR_{AB} + \delta_A)] \exp\left(-\frac{2R_{AB}}{\lambda}\right) \right] \quad (1)$$

where k is the wavenumber of a photoelectron emitted from the x-ray absorbing atom A K edge. R_{AB} and \hat{R}_{AB} are the distance between the atom A and scattering atom B, and its unit vector, respectively, $f_B(k, \pi)$ is the amplitude of the photoelectron back-scattered by B, δ_A is the phase shift of the electron scattered by A, λ is the damping factor stemming from many-body effects and ϵ is the unit vector of the polarization of incident x-rays. When the direction of ϵ is effectively random with respect to \hat{R}_{AB} , then equation (1) can be averaged over ϵ to obtain the ‘non-polarized’ formula

$$\chi(k) = -\text{Im} \left[\sum_B \frac{1}{kR_{AB}^2} f_B(k, \pi) \exp[i2(kR_{AB} + \delta_A)] \exp\left(-\frac{2R_{AB}}{\lambda}\right) \right]. \quad (2)$$

If the effects of static and dynamic disorders are taken into account, we have another damping factor which is a ‘Debye–Waller-type factor’. This effect has been discussed for equation (2) by Beni and Platzman [5] and Sevillano *et al* [6] in terms of the harmonic vibration model. Tranquada and Ingalls (TI) [7] have also discussed it for equation (2) from the anharmonic vibration model in some superionic conductors. Recently we have also studied it using the harmonic and anharmonic models for high- T_c superconductors [8, 9] and also superionic conductors [10]. In these materials, the higher-order cumulant terms play quite an important role.

In an investigation of oriented materials, equation (1) should be used. The purpose of this paper is to obtain the EXAFS Debye-Waller factor for equations (1) and (2) in the cumulant expansion. In section 2, the cumulant expansion is precisely carried out for the polarized and non-polarized EXAFS formulae to obtain an improved damping factor. Section 3 discusses the validity of a superposition rule of the two averages for the cumulant series, with respect to dynamic and static disorders. On the basis of the two previous sections, we give the explicit EXAFS formulae made up of the cumulants to the fourth order in section 4. The spherical wave correction is also attached in these explicit formulae for reference. The improved cumulant is estimated, for example, for CuBr.

2. Cumulant expansion

2.1. Polarized EXAFS

In equation (1), we consider a small deviation of R_{AB} from R_{AB}^0 by

$$u_{AB} = R_{AB} - R_{AB}^0 \quad (3a)$$

$$R_{AB} = R_B - R_A \quad (3b)$$

$$u_{AB} = u_B - u_A \quad (3c)$$

where R_{AB}^0 is the distance of a pair of atoms A and B in the regular lattice now under consideration. If an average value $\langle\langle u \rangle\rangle$ of u is non-zero, we introduce the deviation δu :

$$R_{AB} = R + \delta u \quad (4a)$$

$$R = R_{AB}^0 + \langle\langle u_{AB} \rangle\rangle \quad (4b)$$

$$\delta u = u_{AB} - \langle\langle u_{AB} \rangle\rangle \quad \langle\langle \delta u \rangle\rangle = 0. \quad (4c)$$

The meaning of the average $\langle\langle \rangle\rangle$ will be given explicitly in section 3.

Let us consider the function $F(R_{AB})$:

$$F(R_{AB}) = (\epsilon \cdot \hat{R}_{AB})^2 (1/R_{AB}^2) \exp(2\zeta R_{AB}) \quad (5)$$

$$\zeta = ik - 1/\lambda \quad (6)$$

which is proportional to the B component of the normalized x-ray absorption function $\chi(k)$ in equation (1). If we express the scalar R_{AB} as

$$R_{AB} = R(1 + \delta)^{1/2} \quad (7)$$

$$\delta = 2R \cdot \delta u / R + \delta u^2 / R^2 \quad (8)$$

and equation (5) can be expanded in δ in the form

$$F(R_{AB}) = (\epsilon \cdot \hat{R})^2 (1/R^2) \exp(2\zeta R) G \quad (9)$$

$$G = [1 + (\epsilon \cdot \delta u) / R(\epsilon \cdot \hat{R})]^2 Q \quad (10)$$

$$Q = \sum_{m,n=0}^{\infty} \frac{(2\zeta R)^m}{2^m m!} (-1)^n (1+n) \left(1 - \frac{1}{2^2} \delta + \frac{3!!}{3!2^2} \delta^2 - \frac{5!!}{4!2^3} \delta^3 + \dots \right)^m \delta^{m+n}. \quad (11)$$

When averaging equation (9) over some distribution of δu by observing equation (4c), we retain only the lowest-order terms in δu in each order of $(\zeta R)^m$, such that

$$\begin{aligned} \langle\langle G \rangle\rangle = & 1 + \zeta R \left\{ \left[\langle\langle \delta u^2 \rangle\rangle - 9 \langle\langle (\delta u \cdot \hat{R})^2 \rangle\rangle + 2 \langle\langle (\epsilon \cdot \delta u)(\hat{R} \cdot \delta u) \rangle\rangle / (\epsilon \cdot \hat{R}) \right] / R^2 \right. \\ & \left. + O(u^3) \right\} + (1/2!2^2)(2\zeta R)^2 [4 \langle\langle (\delta u \cdot \hat{R})^2 \rangle\rangle / R^2 + O(u^3)] + \dots \end{aligned} \tag{12}$$

It is also noted that the neglected term $(\epsilon \cdot \delta u)^2$ in the $(2\zeta R)^0$ order is quite small compared with the leading term of $(2\zeta R)^2$ order since the EXAFS formulae (1) and (2) are valid for $kR \gg 1$. Thus we have

$$\langle\langle G \rangle\rangle = 1 + \sum_{n=2}^{\infty} \frac{1}{n!} (i2k)^n \sigma(n) \tag{13}$$

$$\begin{aligned} \sigma(2) = & \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle + i(2/kR)(1 + R/\lambda) \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle \\ & + i(1/2kR) [5 \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle - \langle\langle \delta u^2 \rangle\rangle - 4 \langle\langle (\epsilon \cdot \delta u)(\hat{R} \cdot \delta u) \rangle\rangle / (\epsilon \cdot \hat{R})] \end{aligned} \tag{14}$$

$$\sigma(n) = \langle\langle (\hat{R} \cdot \delta u)^n \rangle\rangle \quad n \geq 3 \tag{15}$$

where it is observed that $k\lambda \gg 1$, $\delta u/R \ll 1$ and $\delta u/\lambda \ll 1$. Equation (13) can now be rewritten in the 'cumulant' expansion form. We call this the cumulant expansion hereafter [7]. Thus equation (1) can be given explicitly by the cumulant series formed of leading terms:

$$\chi(k) = \text{Im} \left[\chi_0(k) \exp \left(\sum_{n=1}^{\infty} \frac{(i2k)^n}{n!} \sigma_{cn} \right) \right] \tag{16}$$

$$\chi_0(k) = - \sum_B (\epsilon \cdot \hat{R})^2 \frac{3}{kR^2} f_B(k, \pi) \exp[i2(kR + \delta_A)] \exp \left(-\frac{2R}{\lambda} \right) \tag{17}$$

$$\sigma_{c1} = 0 \tag{18}$$

$$\sigma_{c2} = \sigma(2) \tag{19}$$

$$\sigma_{c3} = \langle\langle (\hat{R} \cdot \delta u)^3 \rangle\rangle \tag{20}$$

$$\sigma_{c4} = \langle\langle (\hat{R} \cdot \delta u)^4 \rangle\rangle - 3 \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle^2. \tag{21}$$

The n th-order cumulant for $n \geq 3$ turns out to give

$$\sum_{n \geq 3} \frac{(i2k)^n}{n!} \sigma_{cn} = \ln \left(1 + \sum_{n=2}^{\infty} \frac{(i2k)^n}{n!} \langle\langle (\hat{R} \cdot \delta u)^n \rangle\rangle \right) \tag{22}$$

as shown in equations (20) and (21) for reference.

2.2. Non-polarized EXAFS

If we use x-rays with $\epsilon \parallel R$, or if we can average $\epsilon \cdot \delta u$ of equation (14) over ϕ of ϵ where its polar coordinate with respect to R is taken as $(1, \theta, \phi)$, then equation (19) is reduced to

$$\sigma_{c2} = \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle + i(2/kR)(1 + R/\lambda) \langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle + i(1/2kR) [\langle\langle (\hat{R} \cdot \delta u)^2 \rangle\rangle - \langle\langle \delta u^2 \rangle\rangle]. \tag{23}$$

When we directly start from equation (2) and deal with it in the same way as in section 2.1, we again obtain a series expansion of the form of equation (16) but with equations (22), (23) and

$$\chi_0(k) = - \sum_B \frac{1}{kR^2} f_B(k, \pi) \exp[i2(kR + \delta_A)] \exp\left(-\frac{2R}{\lambda}\right). \quad (24)$$

Equations (22) and (23) constitute the correct expansion for the basic EXAFS formula, equation (2), which improves the result obtained by π [7]. The result of π lacks the third term $i[\langle\langle(\hat{R} \cdot \delta u)^2\rangle\rangle - \langle\langle\delta u^2\rangle\rangle]/2kR$ of equation (23).

3. Static and dynamic disorders

Let us consider the average with respect to static and dynamic disorders. The static disorder is now the configuration disorder which does not depend on time, while the dynamic disorder arises from the thermal vibration of atoms. As to the actual average for the dynamic disorder, one can utilize the partition function with the relevant Hamiltonian [5, 6], while for the static disorder we may use, for example, the normal distribution function of δu . The explicit expressions of the averages, however, are not concerned in this paper; so we do not consider them any more.

Corresponding to the above two averages, the deviation can be divided into two parts as

$$\delta u = \delta u_s + \delta u_d. \quad (25)$$

The average now reads

$$\langle\langle \rangle\rangle = \langle\langle \rangle_s\rangle_d \quad (26)$$

where the subscripts *s* and *d* denote the static and dynamic averages, respectively. Thus we have the cumulant composed of two parts:

$$\sigma_{cn} = \sigma_{cn,s} + \sigma_{cn,d}. \quad (27)$$

For example,

$$\sigma_{c4,s} = \langle\langle(\hat{R} \cdot \delta u_s)^4\rangle_s\rangle - 3\langle\langle(\hat{R} \cdot \delta u_s)^2\rangle_s\rangle^2 \quad (28)$$

$$\sigma_{c4,d} = \langle\langle(\hat{R} \cdot \delta u_d)^4\rangle_d\rangle - 3\langle\langle(\hat{R} \cdot \delta u_d)^2\rangle_d\rangle^2. \quad (29)$$

This superposition holds for every cumulant for equation (16) which is composed of leading terms as has been discussed in section 2. If we allow for the higher-order terms in δu in each order of the cumulant, then the cross terms such as $\langle \rangle_d \langle \rangle_s$ appear.

4. Discussion and summary

We have investigated the K EXAFS formulae in terms of the cumulant expansion for both polarized and non-polarized cases. The former formula, when the polarization vector ϵ is taken parallel to the near-neighbour direction R , exactly amounts to three times the latter.

4.1. Non-polarized EXAFS formula

For atoms with highly anharmonic vibrations, the higher-order cumulant becomes naturally important. Superionic materials are quite involved in this case. Taking

CuI as an example, the anharmonic potential of a cubic works fairly well [11, 12]. In the case of CuBr, the potential is considered to be a quartic [7]. Hence it is quite useful to have an explicit expression for the formula to the fourth order in the cumulant expansion. In addition, the lowest-order spherical wave correction in $1/kR$ is introduced.

Now define

$$\xi_{AB} = \xi'_{AB} + i\xi''_{AB} \quad (30)$$

$$\xi'_{AB} = -2k^2 \operatorname{Re} \sigma_{c2} + \frac{2}{3}k^4 \sigma_{c4} - 2p'_B(k)/kR \quad (31)$$

$$\xi''_{AB} = -2k^2 \operatorname{Im} \sigma_{c2} - \frac{4}{3}k^3 \sigma_{c3} + 2p''_B(k)/kR \quad (32)$$

with the aid of equations (20), (21) and (23), where the spherical wave correction to the order $(1/kR)^3$ is given by [3]

$$p'_B(k) + ip''_B(k) = 1 + g_B(k, \pi)/f_B(k, \pi) \quad (33)$$

$$f_B(k, \pi) = \sum_{l=0}^{\infty} f_B(k; l)(-1)^l \quad (34)$$

$$f_B(k; l) = (2l + 1)\{\exp[i2\delta_B(l)] - 1\}/i2k \quad (35)$$

$$g_B(k, \pi) = \sum_{l=0}^{\infty} [l(l + 1)/2] f_B(k; l)(-1)^l \quad (36)$$

$\delta_B(l)$ being the phase shift of the l th partial wave scattered by the atom B. These spherical wave corrections ($O[(kR)^{-3}]$) originate from the two elementary scattering processes, namely the single scattering (by B) and double scattering (by B and A), which are exactly the processes for which equations (1) and (2) ($O[(kR)^{-2}]$) are obtained. For the precise derivation, the reader is referred to [3]. Then, by rewriting $f_B(k, \pi) = |f_B(k, \pi)| \exp(i\phi_B)$ and replacing R by R_{AB} newly redefined, we have the non-polarized EXAFS formula

$$\chi(k) = - \sum_B \frac{1}{kR_{AB}^2} |f_B(k, \pi)| \exp\left(\xi'_{AB} - \frac{2R_{AB}}{\lambda}\right) \sin(2kR_{AB} + 2\delta_A + \xi''_{AB} + \phi_B) \quad (37)$$

including the anharmonic vibrations of relevant atoms to the fourth order in the cumulant. Multiplying equation (37) by the factor 3 gives the formula for the polarized EXAFS with $e||R_{AB}$.

4.2. Evaluation of σ_{c2}

The difference in the cumulant expansion obtained by Π , which has been discussed at the end of section 2, involves equation (37). So it is of interest to see how it works in a quantitative manner. let us discuss only the dynamic disorder.

The difference is the imaginary part of the second-order cumulant σ_{c2} , which contributes to the determination of the near-neighbour distance R as we see from equations (32) and (37). If we neglect the $1/\lambda$ term in equation (23) and simply take $\langle \delta u^2 \rangle_d$ as $3\langle (\hat{R} \cdot \delta u)^2 \rangle_d$, then the effective distance can be given within the second-order cumulant by

$$R_{\text{eff}} = R - \langle (\hat{R} \cdot \delta u)^2 \rangle_d / R \quad (\text{present work}). \quad (38)$$

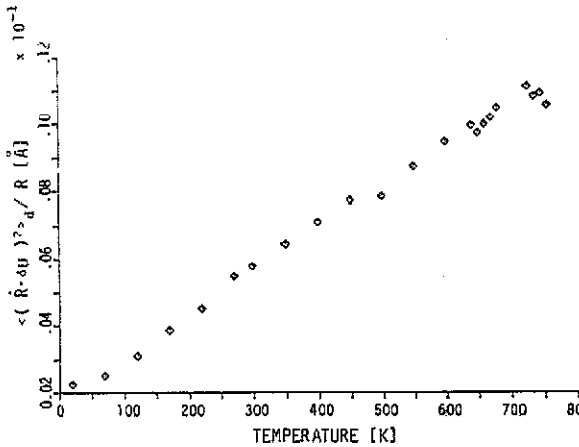


Figure 1. Temperature dependence of $\langle (\hat{R} \cdot \delta u)^2 \rangle_d / R$ for CuBr.

On the other hand, for the expansion obtained by TI we have

$$R_{\text{eff}} = R - 2\langle (\hat{R} \cdot \delta u)^2 \rangle_d / R \quad (\text{TI}). \quad (39)$$

Since R_{eff} is experimentally determined, the distance R is smaller for the present work than the value obtained by TI. In the case of the superionic conductor CuBr at 600 K [10], $\langle (\hat{R} \cdot \delta u)^2 \rangle_d / R \simeq 0.01 \text{ \AA}$, which means that the Br–Cu distance is about 0.01 \AA shorter than the value estimated from equation (39). A full temperature dependence of $\langle (\hat{R} \cdot \delta u)^2 \rangle_d / R$ for CuBr is shown in figure 1, where the analyses have been done for the EXAFS data from the Br K edge [10] by the use of equation (37) without the spherical wave correction. The discussion about the spherical wave correction is beyond the scope of the present paper.

It can be understood that the present cumulant expansion gives rise to a correction of about $1/100 \text{ \AA}$ in the CuBr superionic conductor. However, in materials with weak anharmonicity, the non-polarized EXAFS formula effectively gives the result obtained by TI.

Acknowledgment

We would like to express our hearty thanks to Professor H Maeda for discussion and calculation of figure 1.

References

- [1] Sayers D E, Lytle F W and Stern E A 1970 *Adv. X-ray Anal.* **13** 248
- [2] Lee P A, Citrin P H, Eisenberger P and Kincaid B M 1981 *Rev. Mod. Phys.* **53** 769
- [3] Ishii T 1984 *Prog. Theor. Phys.* **72** 412
- [4] Teo B K 1986 *EXAFS, Principles and Data Analysis* (Berlin: Springer)
- [5] Beni G and Platzman P M 1976 *Phys. Rev. B* **14** 1514
- [6] Sevillano E, Meuth H and Rehr J J 1979 *Phys. Rev. B* **20** 4908
- [7] Tranquada J M and Ingalls R 1983 *Phys. Rev. B* **28** 3520
- [8] Maruyama H, Ishii T, Bamba N, Maeda H, Koizumi A, Yoshikawa Y and Yamazaki H 1989 *Physica C* **160** 524
- [9] Maruyama H, Kimura H, Koizumi A, Yamazaki H, Maeda H and Ishii T 1991 *X-Ray Absorption: Fine Structure* ed S S Hasnain (Chichester, West Sussex: Ellis Horwood) p 370
- [10] Maeda H, Yoshiasa A, Koto K and Ishii T 1990 *Solid State Ion.* **40–41** 345
- [11] Miyake S, Hoshino S and Takenaka T 1952 *J. Phys. Soc. Japan* **7** 279
- [12] Matsubara T 1975 *J. Phys. Soc. Japan* **38** 1076