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Atomic Absorption Background in EXAFS of Rb in Inter-Alkaline Alloys

A. Kodre[1,2,*], I. Arčon[3,2], J. Padežnik Gomilšek[4] and A. Mihelič[2]

[1]Faculty of Mathematics and Physics, Jadranska 19, SI-1000 Ljubljana, Slovenia
[2]J. Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
[3]Nova Gorica Polytechnic, Vipavska 13, SI-5000 Nova Gorica, Slovenia
[4]Faculty of Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

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Abstract

In the room-temperature EXAFS spectrum of Rb in the Rb/K alloy, the sharp spectral features due to double photoexcitation are plainly visible from 40 eV above the K edge. The weak and short structural signal is attributed to the strong thermal disorder. A unique atomic absorption background of the Rb atoms in the solid alloy is extracted and compared to the pure atomic absorption, measured on the monatomic Rb vapor, as a direct test of the practical transferability of experimentally determined atomic absorption backgrounds.

1. Introduction

It is well known in X-ray absorption spectrometry that the EXAFS region above an absorption edge hosts, beside the structural signal, also one or more groups of small sharp features, the multielectron excitations [1–3]. These, together with their extended tails, comprise the so-called atomic absorption background (AAB), characteristic of the target atom but only weakly depending on its environment. In the standard EXAFS analysis, the AAB is approximated by a spline background, constructed from the Fourier components of the absorption signal with periods below the range of possible neighbor distances. This may be adequate for samples with a strong structural signal. For weakly ordered or amorphous substances, however, the structural signal and AAB may be of comparable amplitude with widely overlapping harmonic components so that Fourier separation is not feasible and the analysis can only proceed with a directly determined AAB, exploiting its transferability for a given atomic species [4, 5].

The scarce data on the directly determined AAB come either from experiments on monatomic elemental samples or from the reverse analysis where the structural signal can be removed from the absorption spectrum with sufficient accuracy. The first and the only exact approach provided AABs of alkaline metals [6–9] and Zn [10], Cd [11] and Hg [12], if the data on noble gases could be momentarily put aside for the evident lack of interest from EXAFS practitioners. The second approach is more generally applicable, its early examples may be found in comparative studies using reference standards [3, 13–15].

Absorption spectra of inter-alkaline alloys open another path to AAB, seemingly related to both approaches. The Cs L edge absorption of a Cs/Na alloy at room temperature shows virtually no structural signal [16, 17]. Its atomic character is suggested after comparison with the purely atomic absorption of the adjacent noble gas Xe [18]. In the same way, the Rb K-edge absorption measured on a thin layer of the Rb/K or Rb/Na alloy is almost EXAFS-free, surprisingly similar to the absorption spectrum of the monatomic Rb vapor [6, 8]. In the present study, the absorption of the Rb/K alloy with atomic ratio 1 : 6 is measured at several temperature points between 80 K and room temperature with the aim to establish the temperature dependence of the crystalline order, i.e. to decide whether the absence of the structural signal is caused merely by the thermal disorder or by formation of a specific highly disordered phase.

2. Experiment

The alloys of Rb and Cs with the lighter homologues K and Na in different mixing ratios were prepared by melting together and homogenizing appropriate amounts of the constituent elements under the bath of paraffine oil. A speck of the solid alloy was placed between kapton foils with a drop of the oil, squeezed between carbon platelets in a special container and inserted into the cryostat. The absorption measurement was performed at the BM29 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, with a two-crystal Si(311) monochromator with a resolution of ~0.5 eV at the Rb K edge (15200 eV). The high flux of monochromatic beam and remote vision system of the station with a TV camera and a fluorescent screen was crucial for the success of the experiment, allowing to choose a small patch of homogeneous transmission on the sample.

3. Results and discussion

In view of the weak structural signal of the alloy, the standard spline construction of the absorption background is precluded. Instead, the available AAB, measured on Rb vapor [6, 8], is applied. A similar procedure has been used before for Br and Rb compounds [5] and in the extraction of AAB of 4p elements [15]:

- the data in the pre-edge region are modeled by a sum of a linear function and an arctan profile of the edge: after subtraction of the linear part, the K-shell Rb contribution remains (Fig. 1),
- the K-shell absorption is normalized by a Victoreen fit of the above-edge region beyond 500 eV (i.e. beyond the last visible MPE feature),
- a similarly prepared absorption spectrum of the Rb vapor (cf. insert in Fig. 1) is subtracted, whereby the non-structural contributions are removed,
- the remaining structural signal is transformed into $\chi(k)$ by conversion from E-space to k-space.

In a FEFF model [19, 20] potassium and rubidium are placed as closest neighbors at respective contact distances ($R_{\text{Rb-K}} = 4.72\,\text{Å}$, $R_{\text{Rb-Rb}} = 4.96\,\text{Å}$) [21]. The perfect agreement of the model and experiment is shown in Fig. 2 for the 80 K spectrum

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[*] E-mail: alojz.kodre@fmf.uni-lj.si

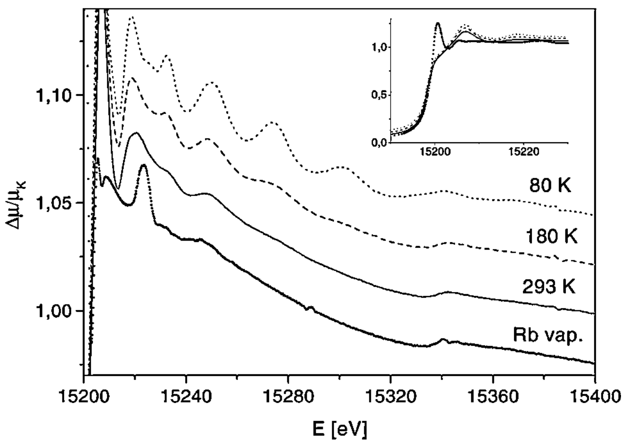

Fig. 1. Normalized K-shell photoabsorption cross-section of Rb in Rb/K = 1 : 6 alloy for three different temperatures, and of Rb vapor. Insert: corresponding K edge profiles to illustrate the procedure of AAB removal. A vertical displacement of 0.03 per spectrum is added for clarity.

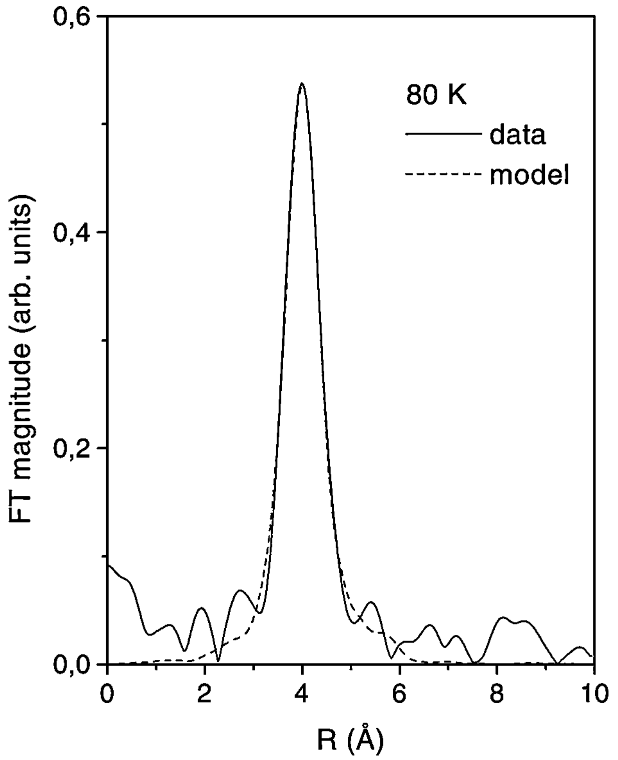

Fig. 2. Fourier transforms of Rb/K EXAFS data and the model (k^3 weight, 1.5 .. 10 Å^{-1}).

Table I. *Parameters of the single-shell model of Rb neighborhood in the Rb/K alloy: shell radius correction ($R_1 = 4.72$Å), the number of K atom neighbors and the Debye-Waller factor. Parameter errors (in parentheses) are given in units of the last decimal place. The N_1 value at 293 K is fixed to stabilize the fit.*

Best fit	Rb/K sample temp. (K)				
parameters	80	130	180	250	293
ΔR_1 (Å)	−0.108(4)	−0.124(4)	−0.131(5)	−0.138(5)	−0.149(6)
N_1	7.5(4)	7.7(5)	8.1(7)	7.2(7)	[8]
$\sigma_1{}^2$ (Å^2)	0.032(3)	0.050(4)	0.069(5)	0.077(5)	0.094(8)

where both neighbor shells are well defined, with $N_K = 7.4 \pm 0.7$ and $N_{Rb} = 2.0 \pm 0.5$. In all other spectra, only the potassium shell is statistically significant: with increasing temperature the EXAFS signal wanes and the weakly populated second shell is drowned in noise. For that reason, a single-shell model is applied to all spectra (Table I). Neglecting the second shell, though, has an unwanted side effect: its vestiges shift the first-neighbor distance (r_1) upwards. Since the second-shell signal wanes with temperature faster than the first-shell signal, r_1 spuriously shows a slight decrease with temperature.

The parameters of the model show a good consistency: the number of neighbors is steady within the error bars, and the Debye-Waller factor grows steadily (practically linearly) with temperature, as expected. It is worth noting that $\sigma^2 = 0.03$ Å^2 at the low-temperature end means a strong suppression of the signal and that value triples within the observed temperature range. The dramatic decrease of the structural signal is thus a purely kinetic effect: no order-disorder phase transition is involved. The large σ^2 value usually affects the accuracy of the other shell parameters: if only one or two oscillations are evident before the interference pattern is suppressed by the thermal motion, the amplitude and phase of the Fourier component cannot be determined with good precision. In the Rb/K alloy, however, the large interatomic distance means a short period of the EXAFS oscillation. Even if the 80 K signal vanishes by ~100 eV above the edge, it completes ~6 cycles and its parameters can be read with sufficient precision.

With the calculated structural signals the atomic absorption background can now be reconstructed. The k-space model signal of FEFFIT [19] is transformed back to the energy space and subtracted from the respective Rb K-shell contribution spectrum of Fig. 1. What remains is the atomic absorption background – but this time specifically the background of the metallic Rb in the alloy. Except for the 80 K spectrum, where the AAB still shows some vestiges of the higher harmonics of the structural signal, the resulting AABs are identical. In Fig. 3, this AAB is compared to the K-edge absorption of the Rb vapor. The difference is minute – the linewidth of the MPE features in the Rb/K AAB is somewhat larger. The [1s4p] peak at 26 eV above the edge is slightly broader and the miniature edges of the 4s and 3d coexcitations at 50 and 130 eV, respectively, are more extended. The additional width can be attributed to the band structure of available final states in the conducting alloy.

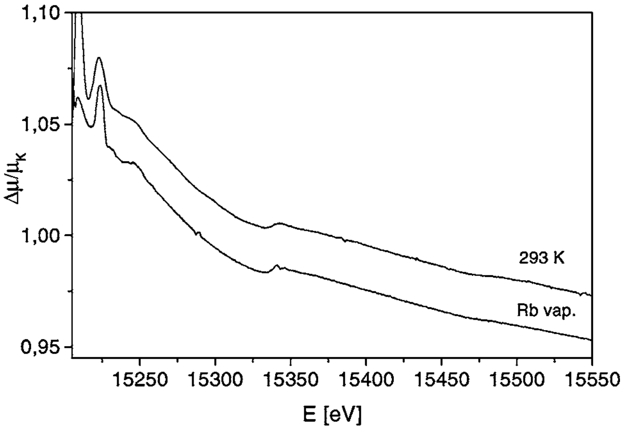

Fig. 3. The comparison of the Rb AAB extracted from the Rb/K alloy spectrum at room temperature, and the atomic absorption on Rb vapor. The signals are vertically displaced by 0.02 for clarity. The artifact on the Rb vapor spectrum at ~15290 eV is a monochromator glitch.

4. Conclusion

The temperature dependence of the Debye-Waller factor shows that the EXAFS signal in the Rb/K alloy is suppressed by the thermal disorder and no specific disordered phase needs to be invoked.

The comparison of the recovered AAB and the Rb vapor absorption exhibits only minute differences in the linewidth and thus proves the transferability of the AABs for the purpose of practical EXAFS analysis.

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