Atomic background in 4p elements

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In the 4p elements from Ga to Kr the atomic background is determined by removing the structural component from simple EXAFS spectra of chalcogenide glasses, solutions and vapors. The background comprises sharp features due to 1s3d and 1s3p multielectron photoexcitations, such as found in the atomic absorption spectrum of gaseous krypton. A spline background, generated by the FEFF "autobk" routine accounts properly for the long-wavelength components, but misses the sharp details of the amplitude of ~1% of the K edge jump. This is sufficient to spoil the structural parameters in EXAFS analysis in some cases.

Atomic absorption background (AB) in the EXAFS spectrum comprises the non-structural components arising from collective excitations of the target atom. Of these, virtual excitations contribute a smooth region of increased slope typically within 80 eV above the absorption edge. Real multielectron excitations introduce sharp features - small resonances, absorption edges, changes of slope, and their combinations - which can extend over several hundreds of eV above the main absorption edge. In the state-of-the-art procedure, realized in the UWXAFS package
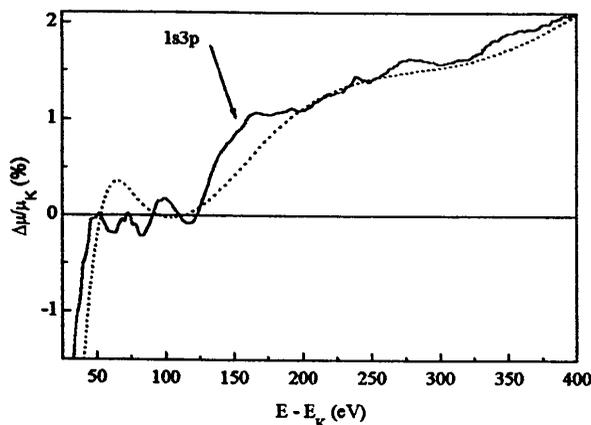
Table I.
The list of the employed samples.

element	sample	
Ga	$6Ge_2S_4$-$4Ga_2S_3$	glass
	$3Ga_2S_3$-Ga_2Te_3	glass
Ge	$9Ge_2S_4$-Ga_2S_3	glass
	$Ge(CH_3)_4$	vapor
	Ge	crystalline
	GeO_2	crystalline
As	AsS	glass
	As	vapor
Se	Se	glass
	Se_7Te_3	glass
Br	KBr	aqueous solution
	CTAB	on carbon black
Kr	Kr	gas

(Stern et al., 1995, Rehr et al., 1992), AB is determined by separation of the long-period components in an EXAFS spectrum. A better approximation of AB is obtained from absorption measurement of free-atom samples, so far available only for noble gases (Schaphorst et al., 1993) and some metal vapors: Na (Tuillier et al., 1982), Hg (Filipponi et al., 1993), Rb (Kodre et al., 1997). The AB of the atom in a compound may differ from that of the free atom, but mainly in the region of ~30 eV above the edge to which ME involving valence electrons are limited. Thus, free-atom AB is perfectly applicable in the region of interest for practical EXAFS analysis.

Due to experimental difficulties in preparation of free-atom samples, an alternative way to determine AB is extraction from beneath the EXAFS signal, preferably from samples with small and simple EXAFS. In this way, AB of an atom in a specific chemical environment can in principle be determined (Li et al., 1992). Since the experimental noise and unresolved structural components cannot be completely eliminated, the result is, as a rule, inferior to the free-atom AB.

In the present work, using a modification of the earlier technique, AB of the 4p elements from Ga to Kr, is determined in the EXAFS region from 60 eV above the K edge onward. Samples with atoms in different environment (gases, solutions, crystalline material - Table I) are used but the main part of experimental material is obtained from structurally similar chalcogenide glasses of elements from Ga to Se. There, the target

Figure 1.
Atomic absorption background in Ge: the initial spline approximation AB^0 (dotted line) and the final result AB^2 (solid line) for GeS_2 glass.
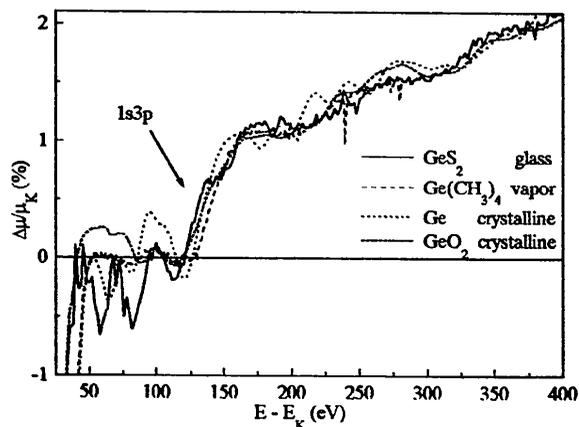
Figure 2.
Comparison of the 1s3p feature in Ge samples.

atom is built into rigid tetrahedral units which are connected into a highly disordered framework (Loireau-Lozac'h et al., 1996, Majid et al., 1997). In this way, the strongest EXAFS components from nearest neighbors are reliably modeled, while the contributions of farther neighbors largely cancel out.

The spline from "autobk" routine is used as the starting approximation AB^0, and eliminated from the absorption spectrum of a glass. The remaining EXAFS signal is fitted to the FEFF model of the tetrahedral unit as in the earlier analysis (Loireau-Lozac'h et al., 1996, Majid et al., 1997) with a minimum number of adjustable parameters: expansion factor, Debye Waller factor and zero energy. Complete relaxation of the model is not allowed, to prevent the components of the AB from getting absorbed into slightly shifted structural components. The difference AB^1 of the original EXAFS spectrum and the fitted model represents the new approximation to the AB. It is used on the EXAFS spectrum of a different sample of the target atom where the procedure is repeated. The resulting background AB^2 can in most cases be accepted as the final result since further iterations yield but little improvement.

The procedure is illustrated in Fig 1 for the case of Ge where EXAFS spectra of GeS_2 and $Ge(CH_3)_4$ were used. The comparison between the spline AB^0 and the final result AB^2 shows that the spline approximates correctly the smooth part of the background, but, understandably, misses the sharp features. In Fig 2, the AB^2 obtained from widely different Ge samples demonstrate, within the relatively large noise level stemming from residual structural components, that the sharp step of 1% magnitude at 150 eV above the K edge, and a subsequent change of the slope, is indeed an inherent feature of Ge atom absorption. It can be attributed mainly to the shake-up transition to the [1s3p]4p state, with contributions of some resonant excitations, the [1s3p]5p shake-up and [1s3p] shakeoff.

The results of the procedure for the entire series of elements, together with the direct measurement of the AB on krypton, are shown in Fig 3. A systematic progression of the 1s3p feature in size and energy is observed; similarly, the 1s3d feature enters the EXAFS region and is reliably resolved in Se, Br and Kr. The

corresponding Dirac-Fock energies are indicated by arrows. The 1s3p feature can be decomposed into channel contributions by a model based on the analysis of Kr [Schaphorst et al., 1993] and Rb (Arčon et al., 1997). The magnitude of the [1s3p]4p shake-up channel (Fig 4) exhibits a linear trend following the number of the empty states in the filling 4p subshell.

Although the spline background can satisfactorily follow the overall shape of the AB seen in Fig 1, the sharp 1s3p edge with magnitude of 1% for Ga, Ge, and As introduces harmonic components which can affect the reliability of the EXAFS structural analysis, particularly in disordered samples with weak EXAFS. The 1s3d edge can interfere with EXAFS analysis in Se and Br.

The present work, concentrating on the sharp features in the AB and their effect on EXAFS analysis, cannot be used to test the recently proposed concept of AXAFS (Rehr et al., 1994) which predicts a specific change in smooth, long-period components to AB with the effective radius of the target atom. For the purpose of test, the comparison of AB from samples of an element in essentially different oxidation states and coordination is required. The similarity of the extracted AB and the direct measurement on Kr, however, indicates that multielectron excitations offer a satisfactory explanation for the AB shape.
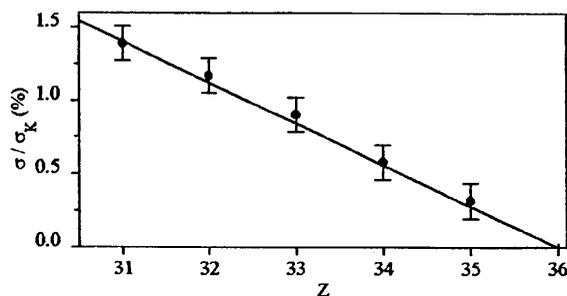
Figure 4.
Relative amplitudes of the [1s3p]4p shakeup channel in 4p elements.

Figure 3.
Atomic absorption background in 4p elements.

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