Journal of Physics: Conference Series **190** (2009) 012063 doi:10.1088/1742-6596/190/1/012063

Femtometer accuracy EXAFS measurements: isotopic effect in the first, second and third coordination shells of germanium

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Abstract. The analysis of the EXAFS signals from ^{70}Ge and ^{76}Ge has evidenced the low-temperature effect of isotopic mass difference on the amplitude of relative atomic vibrations. This effect is reflected in the difference of the Debye-Waller factors of the first three coordination shells, and on the difference of nearest-neighbour average interatomic distances, evaluated with femtometer accuracy. The experimental results are in agreement with theoretical expectations.

1. Introduction

In the last years, the XAFS experimental techniques have undergone remarkable developments: experiments with unprecedented accuracy under extreme conditions of high pressure and temperature, that were not even conceivable just a few years ago, can nowadays be performed. New applications, stimulated by accurate experimental temperature-dependent XAFS measurements on Ge, Ag_2O and ReO_3, can be carried out [1-4]. In parallel with the experimental techniques, XAFS theory and data analysis [5-6] have made considerable progress. Femtometer accuracy in the determination of interatomic distances is now attainable, at least in particular cases [7-9]. Recently, Pettifer et al. [7-9] presented EXAFS measurements of atomic displacements at femtometer scale.

The accuracy of absolute distances evaluated from EXAFS spectra depends on the accuracy of calculated scattering amplitudes and phase shifts, and is typically not better than 0.01 Å. A much better accuracy can however be achieved from the relative comparison of distances, where scattering amplitudes and phase shifts cancel out. Subpicometer accuracy (routinely 10^{-3} Å [2-4] and in some cases 10^{-4} Å [1]) can be attained in thermal expansion studies performed with standard transmission measurements. Femtometer accuracy has been recently obtained with a dispersive spectrometer, without moving components [7-9].

One particularly interesting application is the study of isotopic effects. Recently, we measured temperature-dependent EXAFS on the two isotopes ^{70}Ge and ^{76}Ge [1]. The analysis

of the first coordination shell has evidenced the effect of isotopic mass difference on the low-temperature difference of Debye-Waller (DW) factors, and on the difference of nearest-neighbor average interatomic distances, measured with femtometer accuracy. The analysis has now been extended to the second and third coordination shells, where a contribution of multiple-scattering (MS) effects into EXAFS signal is expected. In this paper, a global account of the results is given.

2. Experimental and data analysis.

Two highly isotopically enriched Ge samples with the degrees of enrichment 98.2% for ^{70}Ge and 99.9% for ^{76}Ge, produced at the Kurchatov Institute, were used. EXAFS measurements have been done at the beam line BM29 of ESRF (Grenoble, France). The EXAFS spectra were measured in the energy range 10900–13500 eV in standard transmission mode.

A Si(111) double-crystal monochromator was used, and harmonic rejection was achieved by 30% detuning. The EXAFS region was sampled at constant photoelectron wave number steps Δk=0.026 Å^{-1}. The stability and reproducibility of energy axis $\Delta E/(E_{max}-E_0)$ of about 10^{-4} (E_o - photoelectron zero energy, E_{max} - photoelectron maximum energy in XAFS) guarantees an accuracy of 10^{-4}Å (10 *femtometer*) and consequently $\Delta R/R$ of the order of 10^{-4} in the determination of variation of interatomic distances (R).

EXAFS signals and Fourier transforms (FT) of the ^{70}Ge isotope at 20 and 300 K are shown in figure 1, left panel. The difference in the EXAFS signals and in the magnitude of FT of the two isotopes at 20 K (right panel of figure 1) is reproducible for all pairs of compared files and different FT parameters utilized.

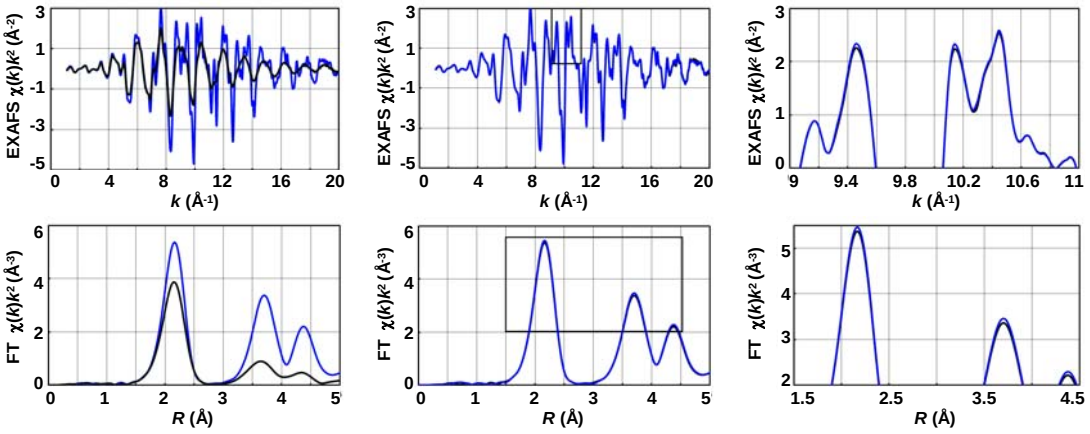

Figure 1. (Color online) EXAFS signals and modulus of Fourier transforms for ^{70}Ge at 20 and 300 K (from top to bottom in the upper panel) and comparison between the EXAFS signals and the Fourier transforms of ^{76}Ge (solid line) and ^{70}Ge (dotted line) at 20 K.

Let us now consider the temperature dependence of the average nearest-neighbour distance <R>. The results of the first-shell analysis performed with experimental phases and amplitudes (semi-empirical approximation) have been presented in the previous paper [1], where the temperature dependencies of average distance <R>, third cumulant and DW factor σ^2 of the two isotopes were separately evaluated. Since the changes in the lattice constant (a) due to temperature are larger than the changes due to the isotopic composition [10, 11], the variation of the difference between averages distances for the two isotopes can be determined using a differential analysis, through a direct comparison of the two isotopes at each temperature. Thus we have obtained the differences in interatomic distances and DW factors between the two isotopes; the difference of third cumulants was negligible.

Figure 2 compares the difference of average interatomic distances for the first-shell, determined by EXAFS, with the difference of distances between average positions determined by X-rays backscattering. The difference between the results of the two

techniques can be attributed to the effect of relative thermal vibrations perpendicular to the Ge-Ge interatomic bond.

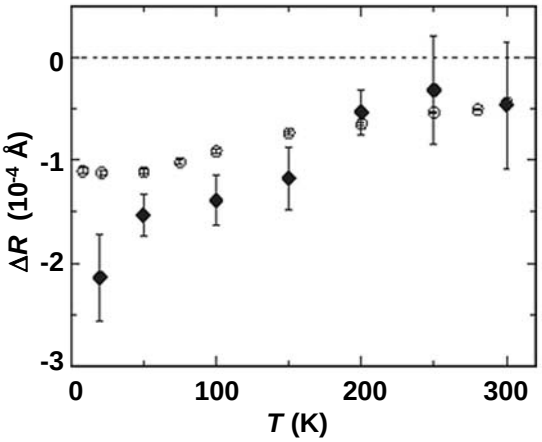

Figure 2. Difference of the nearest-neighbors average interatomic distance in ^{76}Ge and ^{70}Ge, determined from EXAFS analysis (diamonds), compared with the difference of distance between average positions determined from x-ray backscattering [11] (open circles, containing the error bars).

Since the EXAFS signals of the second and third coordination shells are overlapped and contain multiple-scattering (MS) contributions, the analysis has been done with theoretical phases and amplitudes calculated by the FEFF8 code [12, 13] within the single-scattering (SS) and MS approximations. The calculations of scattering amplitude and phase functions were performed for a cluster representing a part of the Ge crystal having a radius of 8 Å. The cluster potential, of muffin-tin (mt) type with the radii R_{mt}(Ge)=1.408 Å, was calculated in a self-consistent way. The complex Hedin-Lundqvist exchange-correlation potential was used to account for inelastic effects.

The program FEFFIT [14] has been used to fit the experimental spectra, and the values of the DW factors have been obtained within the following approximations:

(a) Only DW factors (σ_1, σ_2, σ_3) for single-scattering contributions from the first, second and third coordination shells were considered as independent, the DW factors for 4 relevant MS contributions, i.e. for two double-scattering (DS) and two triple-scattering (TS) paths, were evaluated as linear combinations of the DW values for the SS paths. The DW factors σ_4^2 and σ_5^2 for the DS paths $Ge_0 \rightarrow Ge_1' \rightarrow Ge_1'' \rightarrow Ge_0$ and $Ge_0 \rightarrow Ge_1 \rightarrow Ge_2 \rightarrow Ge_0$, respectively, were set to $\sigma_4^2=\sigma_5^2=\sigma_1^2+\sigma_2^2/2$, and the DW factors σ_6^2 and σ_7^2 for the TS paths $Ge_0 \rightarrow Ge_1 \rightarrow Ge_0 \rightarrow Ge_1 \rightarrow Ge_0$ and $Ge_0 \rightarrow Ge_1 \rightarrow Ge_2 \rightarrow Ge_1 \rightarrow Ge_0$, respectively, were set to $\sigma_6^2=\sigma_7^2=2\sigma_1^2$. Here Ge_0 is the absorbing atom, Ge_1' and Ge_1'' denote two different atoms in the first coordination shell, and Ge_2 denotes the atom in the second coordination shell.

(b) The experimental signal was Fourier filtered, taking into account the contributions with path-lengths in the range from $2xR_1$ to 2x4.5 Å; different values of R_1 have been used in order to include or exclude the first coordination shell.

(c) The upper limit of the wavenumber k was set to 18.0 Å^{-1}, the lower limit was varied from k_1 to k_2 with a step 0.05 Å^{-1}. The result, used in the further analysis, was obtained by averaging the values of DW factors, obtained for each interval of wavenumbers. Different values for k_1 and k_2 have been used, in order to minimize the influence of (i) larger noise at high values of wavenumber, (ii) imperfections in the EXAFS theory at small values of wavenumbers and (iii) MS contributions.

(d) The values of DW factors, obtained for different sets of fitting parameters, were averaged. As there were at least two experimental spectra for each temperature, the values of DW factors, corresponding to different spectra, were also averaged.

(e) Uncertainty bars were determined by cross comparing different data files measured at the same temperature and varying the Fourier filtering and the fitting parameters within reasonable intervals.

The temperature dependencies of DW factors were approximated by the Einstein model, and the corresponding Einstein frequencies were estimated through a best fit procedure.

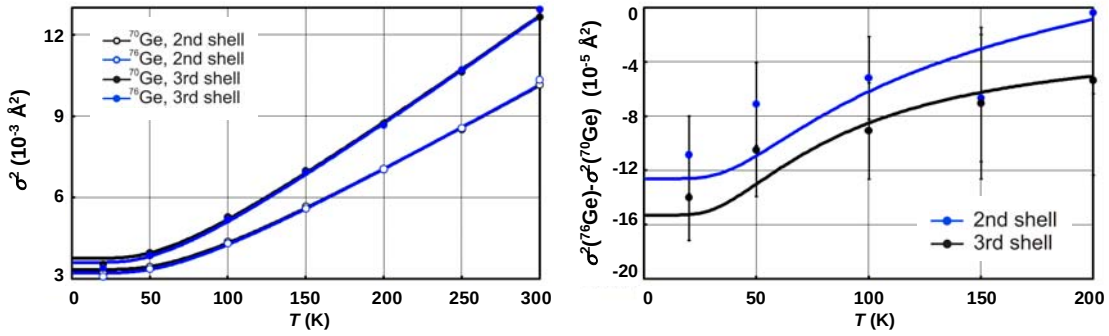

Figure 3. (Color online) Left panel: Temperature dependence of the EXAFS DW factors for the two isotopes ^{70}Ge and ^{76}Ge in the second and third coordination shells. The lines are the best fitting Einstein models for ^{70}Ge and ^{76}Ge. Right panel: Difference of the DW factors for the two isotopes in the second and third coordination shells; the solid lines are the differences between two Einstein models with the same values of the k_0 constant.

3. Results and discussion

The interpretation of the isotopic effect on the DW factors σ^2 for the second and third coordination shells has been done in a similar way as for the first shell [1]. Briefly, the temperature dependence of σ^2 is the sum of the contributions of all normal modes [1]. It can, however, be satisfactorily reproduced by a simple Einstein model:

$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_BT}\right)$$

where each Einstein frequency ω_E (different for different shells) is connected to an effective force constant k_0 through $\omega_E = (k_0/\mu)^{1/2}$ (μ is the reduced mass and k_B the Boltzmann constant). The force constants k_0 are expected not to depend on the isotopic composition, thus it is convenient to express the Einstein model in terms of only k_0 and μ. For low temperatures $T \to 0, \sigma^2 \to \sigma_0^2 = \hbar/2\sqrt{\mu k_0}$, the DW factors depend on the isotopic composition. For high temperatures, $T \to \infty, \sigma^2 \to \sigma_\infty^2 = k_BT/k_0$ (classical behavior) the DW factors are independent of isotopic composition. One thus expects the isotopic effect to influence the zero-point value of σ^2, and progressively disappear when temperature increases.

Let us first consider the DW factors σ^2 of the two isotopes separately (figure 3, left panel). At high temperatures, the Einstein models asymptotically tend to the classical linear behavior, independent of mass. At low temperatures, the isotopic effect is clearly evidenced. Note that in previous semi-empirical analysis of the first shell [1] the absolute values of DW factors have been obtained by fitting Einstein models to the experimental temperature dependence of both samples. In the present analysis with theoretical phases and amplitudes (FEFF8) the absolute values are obtained automatically.

The DW difference $\sigma^2(^{76}\text{Ge})$-$\sigma^2(^{70}\text{Ge})$, obtained from the direct comparison of the experimental data of the two isotopes at each temperature, is shown in the right panel of figure 3. Finally, figure 4 shows the comparison of the results between the MS and SS approximations.

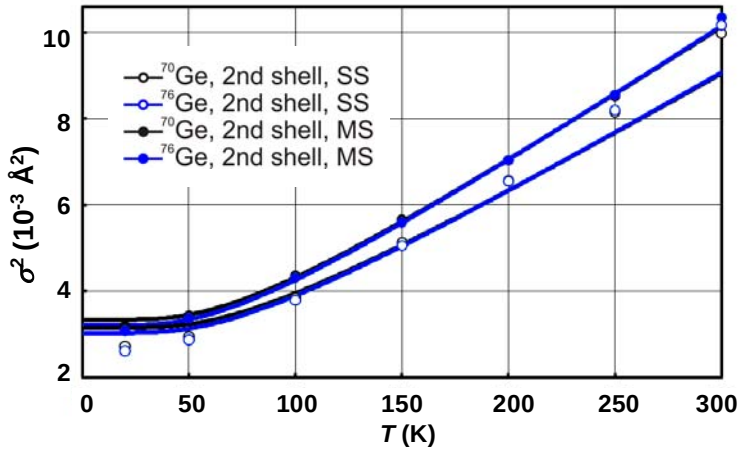

Figure 4. (Color online) Temperature dependence of the EXAFS DW factors for the two isotopes ^{70}Ge and ^{76}Ge in the second coordination shell fitted within the SS and MS approximations. The lines are the best fitting Einstein models for ^{70}Ge and ^{76}Ge.

Table 1. Comparison between ^{70}Ge and ^{76}Ge Einstein frequencies for the second and third coordination shells obtained within harmonic single-scattering and multiple-scattering approximations as well as anharmonic approximation (from [16]).

	$\omega_E\left(^{70}\mathrm{Ge}\right)$, THz		$\omega_E\left(^{76}\mathrm{Ge}\right)$, THz		$\dfrac{\omega_E\left(^{70}\mathrm{Ge}\right)-\omega_E\left(^{76}\mathrm{Ge}\right)}{\bar{\omega}_E}$		Predicted ω_E for natural Ge, THz		Experimental ω_E for natural Ge (SS) [16], THz	
	MS	SS	MS	SS	MS	SS	MS	SS	Harmonic	Anharmonic
2nd shell	4.29	4.55	4.10	4.35	**4.5%**	**4.5%**	4.12	4.37	4.27 ± 0.20	3.90 ± 0.20
3rd shell	3.81	4.02	3.66	3.86	**4.0%**	**4.1%**	3.67	3.87	3.84 ± 0.20	3.48 ± 0.20

The Einstein frequencies for the second and third coordination shells are summarized for two Ge isotopes in table 1. Besides the trivial dependence of the phonon energies on the average isotopic mass [15], the Einstein frequency increases when the isotope mass number decreases through the relationship $\omega_E = \left(k_0/\mu\right)^{1/2}$. Therefore, the expected normalized difference between Einstein frequencies due to isotopic effect should be the same for all coordination shells

$$\frac{\omega_E\left(^{70}Ge\right)-\omega_E\left(^{76}Ge\right)}{\bar{\omega}_E}=\sqrt{\frac{\bar{\mu}}{\mu\left(^{70}Ge\right)}}-\sqrt{\frac{\bar{\mu}}{\mu\left(^{76}Ge\right)}}\approx 4.1\%\,.$$

For the first coordination shell [1]:

$$\omega_E\left(^{70}\mathrm{Ge}\right)=\left(7.70\pm0.02\right)\mathrm{THz},\ \omega_E\left(^{76}\mathrm{Ge}\right)=\left(7.39\pm0.02\right)\mathrm{THz},\ \frac{\omega_E\left(^{70}\mathrm{Ge}\right)-\omega_E\left(^{76}\mathrm{Ge}\right)}{\bar{\omega}_E}\approx 4.1\%\,.$$

The expected difference between zero-point values of DW factors $\left[\sigma^2\left(^{76}\mathrm{Ge}\right)-\sigma^2\left(^{70}\mathrm{Ge}\right)\right]/\sigma^2\left(\mathrm{Ge}\right)$ normalized on medium value should be also the same 4.1% for all coordination shells. The zero-point values of experimental data and Einstein models, $\sigma_0^2=\hbar/2\sqrt{\mu k_0}$ were are only slightly different for the first shell [1], the normalized ratio $\sigma_0^2\left(^{70}\mathrm{Ge}\right)/\sigma_0^2\left(^{76}\mathrm{Ge}\right)$ being about 1.038 and 1.042 for experimental and theoretical Einstein models, respectively. In the present analysis, the normalized ratio $\sigma_0^2\left(^{70}\mathrm{Ge}\right)/\sigma_0^2\left(^{76}\mathrm{Ge}\right)$ is

1.034 and 1.037 for the second and third coordination shells, respectively, in good agreement with the predicted values.

Finally, table 1 shows the comparison of the results between the MS and SS approximations. In spite of the MS contributions we have obtained the reasonable results for the ratio of the Einstein frequencies also in the SS approximation (4.5% and 4.1% for the second and third coordination shells, respectively), but the absolute values are a little overestimated.

4. Conclusions

The temperature dependent measurements on Ge isotopes show that the isotopic effect can be detected by EXAFS. The most direct result is the high sensitivity to the difference of the amplitudes of nearest-neighbors relative vibrations (parallel mean square relative displacement), which has been analyzed with high accuracy from 20 K to 300 K, using experimental phases and amplitudes for the first coordination shell, and using theoretical phases and amplitudes and taking into account multiple scattering effects for the second and third shells. The isotopic effect has been revealed also in the first-shell thermal expansion, demonstrating that the 10 femtometer "barrier" is now attainable with differential analysis, even though such determination is far from trivial and needs the experimental phases and amplitudes in the single-scattering approximation.

Acknowledgments: The authors acknowledge ESRF for provision of synchrotron radiation facilities and support (project HS-2960), as well as the staff of the BM29 beamline for technical assistance. This work was partially supported by Latvian Government Research Grant No. 09.1191 and 09.1211.

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