Baltic School on Application of Neutron and Synchrotron Radiation in Solid State Physics and Material Science (BSANS-2012)

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X-RAY ABSORPTION STUDIES OF LOCAL STRUCTURE WITH FEMTOMETER ACCURACY

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Synchrotron Radiation XAFS studies: Present Status and Future Perspectives

Femtometer-XAFS - experiments with unprecedented accuracy

Nanometer-XAFS - experiments with nanoscale lateral resolution

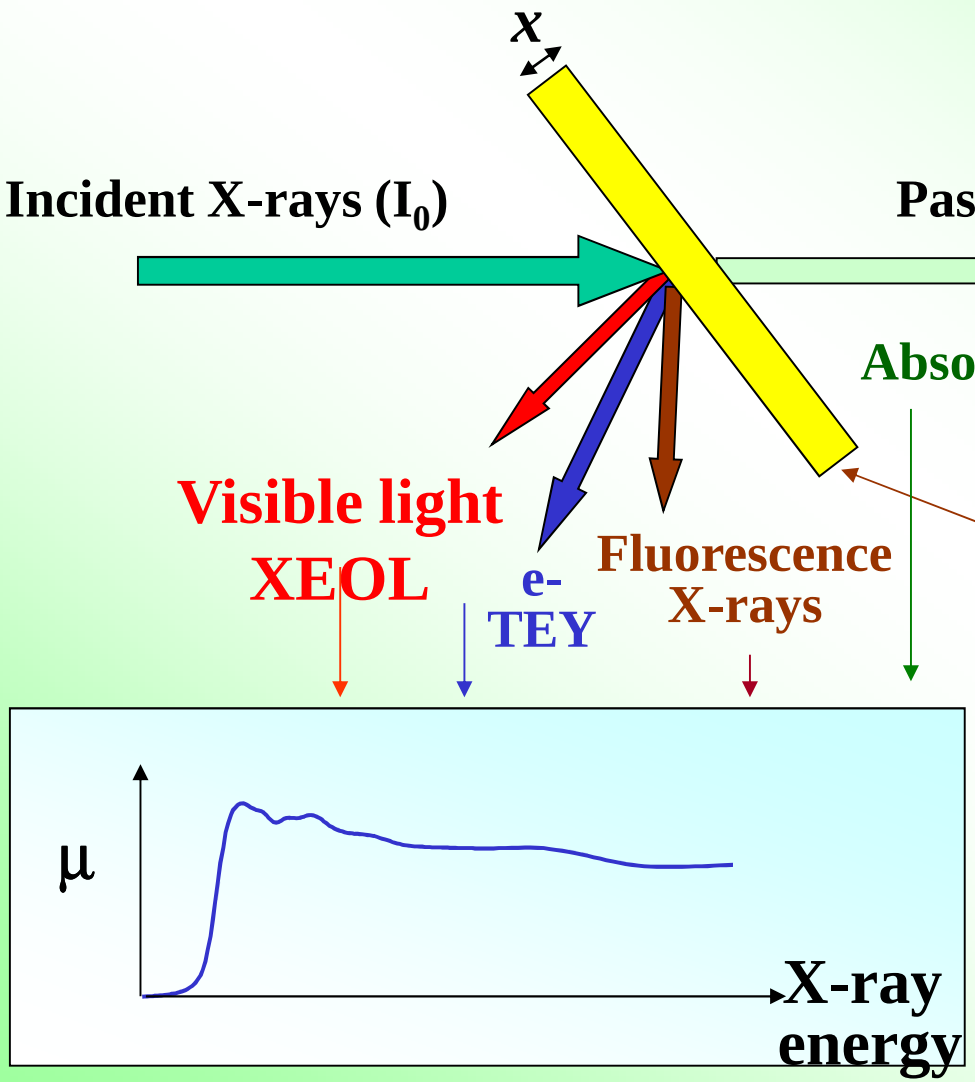
Femtosecond-XAFS – time resolved experiments

X-ray Magnetic Circular Dichroism (XMCD) experiments

XAFS experiments under extreme conditions

In parallel with the experimental techniques, XAFS theory and data analysis have made considerable progress.

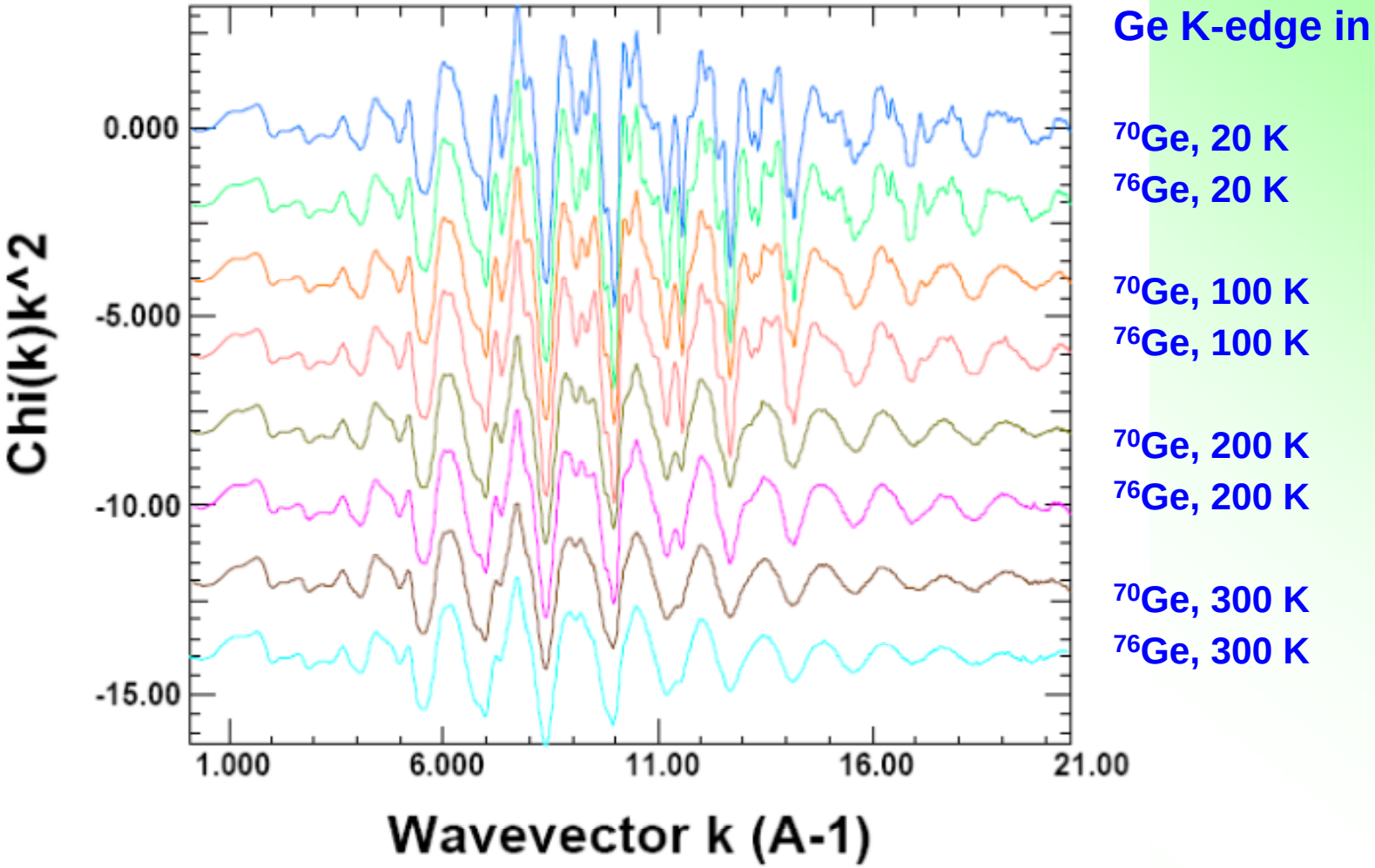
X-ray Absorption Spectroscopy



SAMPLE:

- **solid**
  - **single-crystal**
  - **polycrystalline powder**
  - **glass**
  - **thin film**
- **liquid**
- **gas**

Temperature dependence of EXAFS signals for Ge isotopes 70 and 76



Ge K-edge in

^{70}Ge, 20 K
^{76}Ge, 20 K

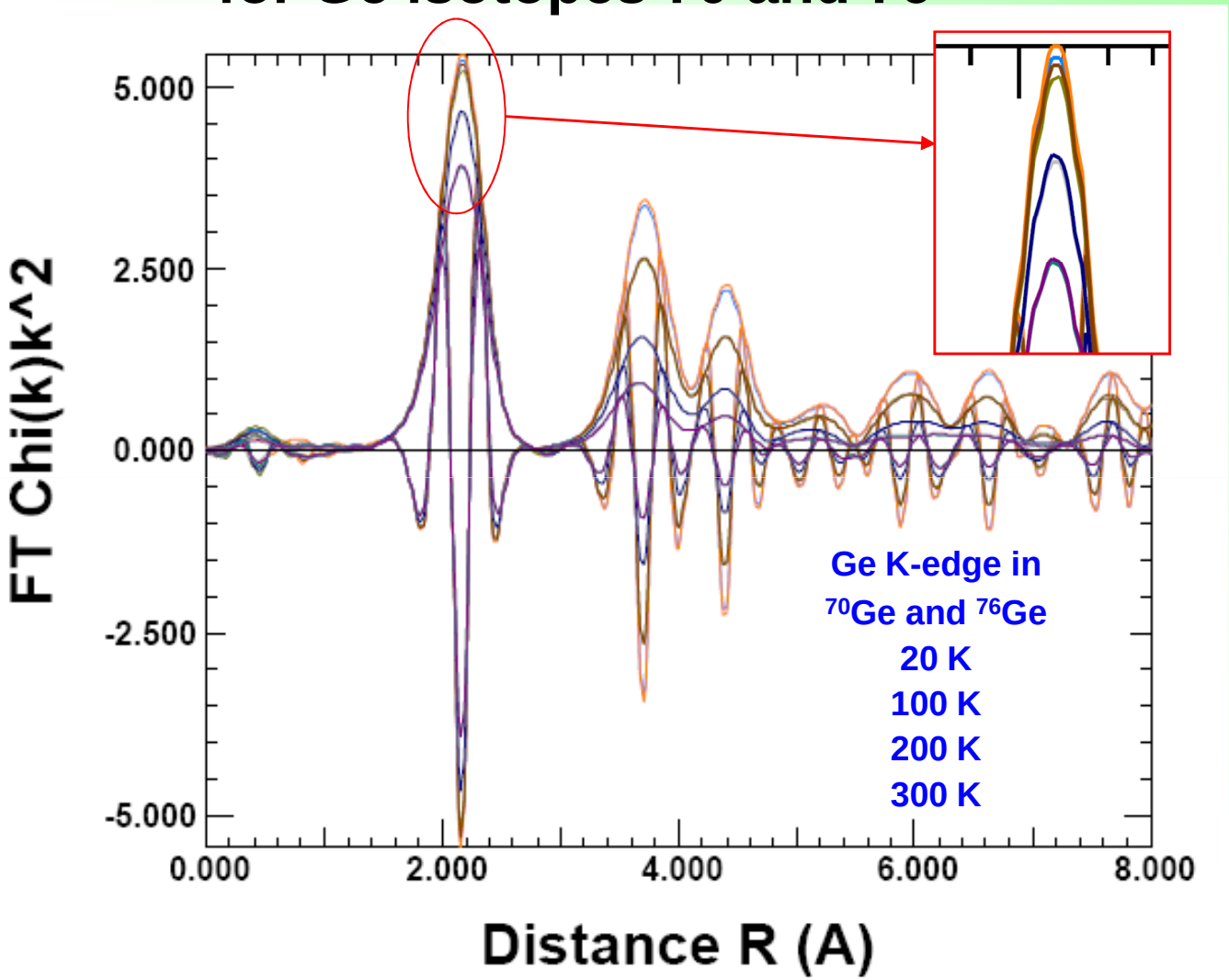
^{70}Ge, 100 K
^{76}Ge, 100 K

^{70}Ge, 200 K
^{76}Ge, 200 K

^{70}Ge, 300 K
^{76}Ge, 300 K

Very good quality signal was measured up to k=21 Å^{-1}.

Temperature dependence of FT EXAFS signals for Ge isotopes 70 and 76



Difference between two Ge isotopes are visible at low temperatures.

Basic Information Obtainable from EXAFS Studies

experiment => *ab-initio* theoretical calculations => data analysis

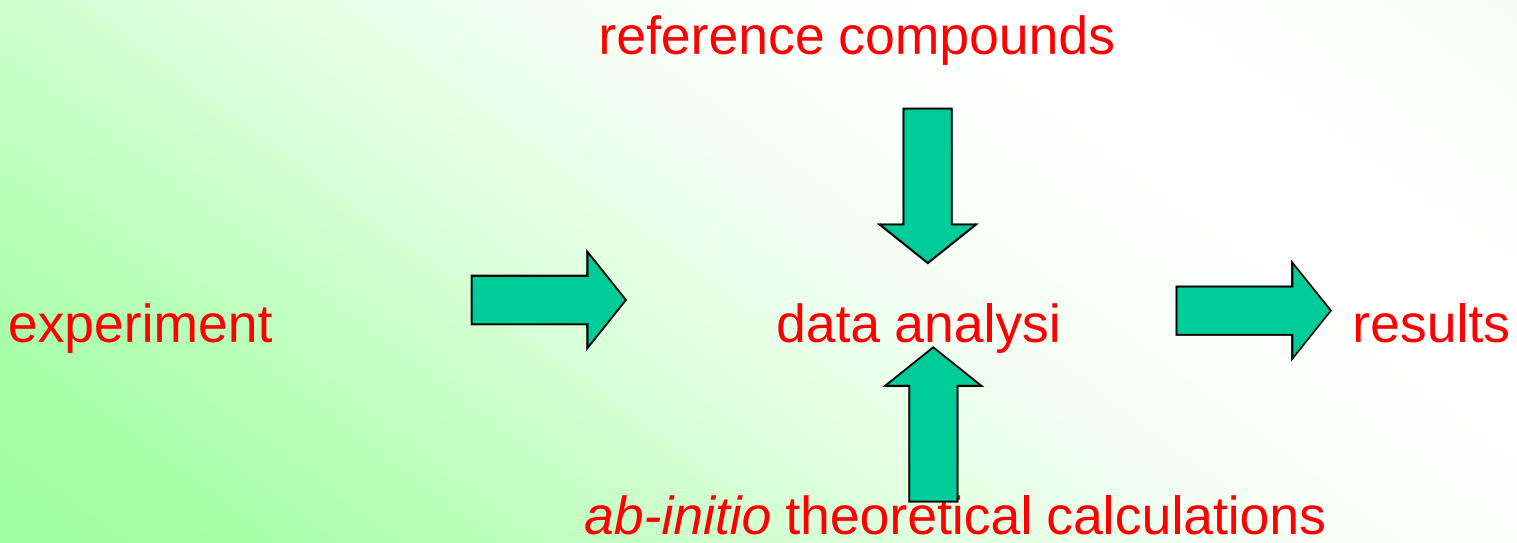
- The number of atoms surrounding the absorber atom (± 5-20%)
- The absorber-scatterer distances (ideally ± 0.01Å for the first shell)
- Atomic disorder data from Debye-Waller terms
- Ligand geometries from multiple scattering
- ….

•Despite of XAFS technique overall success, the *pico-meter* barrier (10^{-2}Å) exists in XAFS spectroscpy:

SUBPICOMETER BARRIER IN XAFS STUDY

Differential technique is particularly effective when temperature, pressure, concentration etc. dependent measurements are performed and only relative values are studied :

- excellent S/N ratio in the range k=1.0-20.0 $Å^{-1}$
- energy reproducibility of 0.01 eV, give rise to a subpicometer accuracy of 10^{-4} Å
- cumulant method



Femtometer accuracy

isotopic effect on EXAFS and isotopic effect on the lattice dynamics and anharmonic properties of Ge^{70} and Ge^{76} (see [1] and Highlight ESRF 2008);

materials with negative thermal expansion as ReO_3, AgO_2, etc. (see [2] and Highlight ESRF 2006);

materials with Jahn-Teller (JT) effect, small radium polaron (WO_3) or with charge disproportionation as $SrFe_xTi_{1-x}O_3$ (see [3] and Highlight ESRF 2007);

Solid solutions as $SrFe_xTi_{1-x}O_3$, $Th_{1-x}U_xO_2$ etc. (see [3,4] and Highlight ESRF 2007).

1. J.Purans, N. D.Afify, G.Dalba, R.Grisenti, S.De Panfilis, A.Kuzmin, V.I.Ozhogin, F.Rocca, A.Sanson, S. I. Tiutiunnikov, P.Fornasini, *Phys.Rev.Lett.*, 100 (2008) 00055901.

2. J. Purans, G. Dalba, P. Fornasini, A. Kuzmin, S. De Panfilis and F. Rocca, XAFS and XRD studies with subpicometer accuracy: The case of ReO_3, *AIP Conf. Proc.* 882 (2007) 422.

3. M. Vračar, A. Kuzmin, R. Merkle, J. Purans, E. A. Kotomin, J. Maier and O. Mathon, *Phys. Rev. B* 76 (2007) 174107.

4. J.Purans, S.Hubert, G.Heisbourg, N.Dacheux, Ph.Moisy, *Inorg. Chem*. 45 (2006) 3887.

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2005 => 1 fm (10^{-5} Å)

Measurement of femtometre-scale atomic displacements by X-ray absorption spectroscopy

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The frequencies of extended X-ray absorption fine-structure (EXAFS)[1] measurements, which are oscillations occurring on the high-energy side of an X-ray absorption edge, can be used to identify interatomic distances in materials. We have used a dispersive X-ray spectrometer[2–5], which has no moving components, to make rapid measurements with minimal energy drift of the difference in EXAFS from the Fe K edge in an iron-cobalt thin film undergoing periodic strain through magnetostriction[6,7]. We show that magnetostriction can be detected by differential X-ray absorption. The magnitude of the recorded signal relative to the noise shows a sensitivity to mean differential atomic motion of one femtometre: a factor of 100 times more sensitive than that normally available[8,9].

EXAFS with Femtometer Accuracy
2004-2008 => 5-10 fm (10^{-4} Å)

PRL **100,** 055901 (2008) PHYSICAL REVIEW LETTERS week ending 8 FEBRUARY 2008

Isotopic Effect In Extended X-Ray-Absorption Fine Structure of Germanium

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(Received 15 October 2007; published 8 February 2008)

Extended x-ray absorption fine structure has been measured on two powdered samples of ^{70}Ge and ^{76}Ge as a function of temperature from 20 to 300 K. The effect of isotopic mass difference on the amplitude of relative atomic vibrations is neatly evidenced by the temperature dependence of the difference of Debye-Waller factors. The isotopic effect is also detected on the difference of nearest-neighbor average ineratomic distances, thanks to a resolution better than 10 fm.

The XAFS was interpreted using backscattering phases and amplitudes obtained in the two different approaches: theoretical and experimental

The **theoretical** backscattering amplitudes **$f(\pi,k)$** and phases **$\phi(\pi,k)$** were calculated by the FEFF6,8 code for the clusters, that mimic the possible environment of Me^{+n} impurity defect. The use of the theoretical amplitudes and phases leads to absolute values of determined structural parameters.

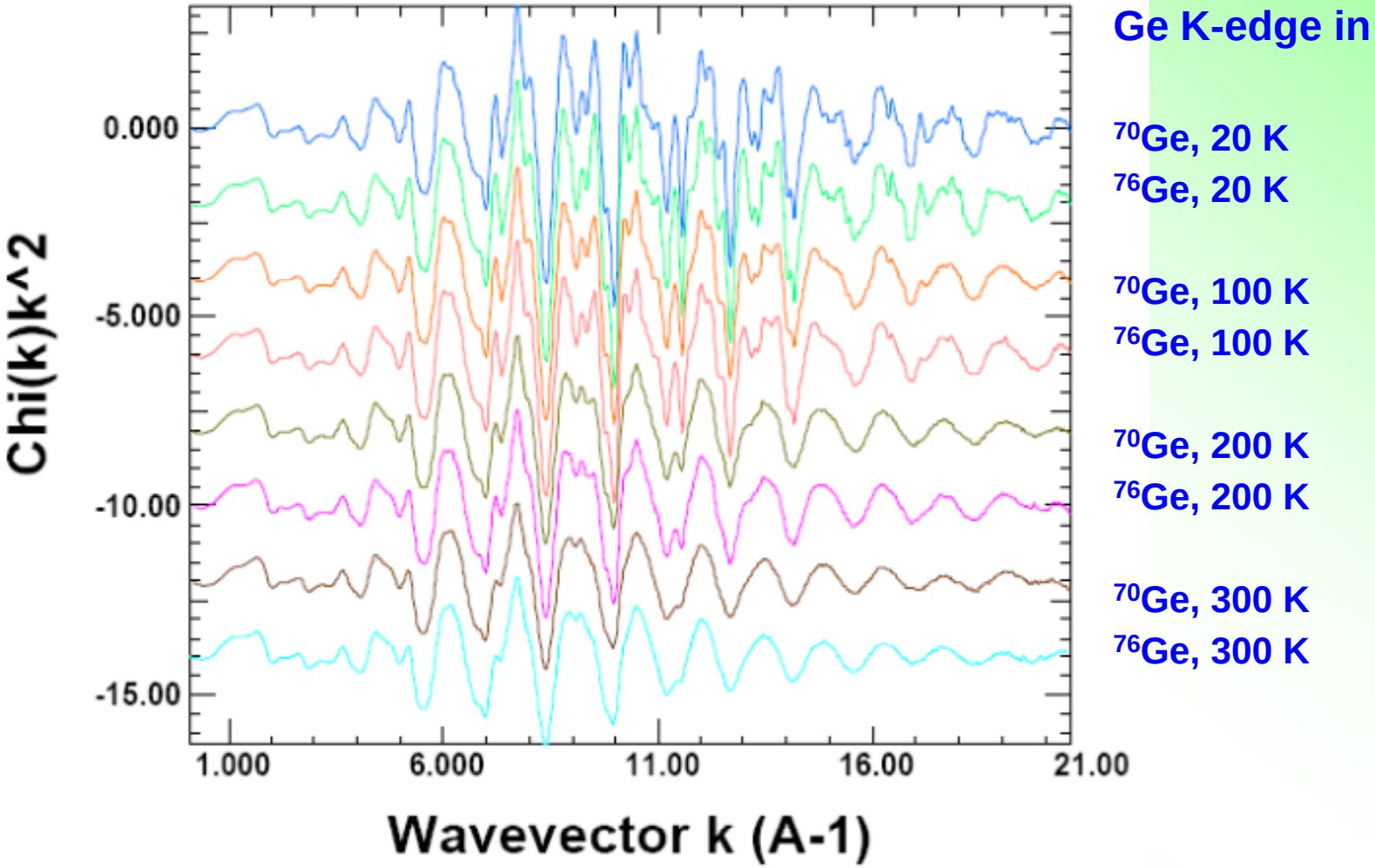
Experimental amplitudes **$f(\pi,k)$** and phases **$\phi(\pi,k)$** were extracted from the experimental XAFS data obtained on reference crystalline sample or solution. Note that experimental amplitudes **$f(\pi,k)$** include the mean free path correction and the multi-electron amplitude reduction factor S^2_0. The use of the experimental amplitudes and phases leads to relative values of determined structural parameters.

Experiment

EXAFS measurements have been carried out at the European Synchrotron Radiation Facilities (ESRF) at the beamline BM-29. The synchrotron radiation was monochromatized using the Si(111) double-crystal monochromator and harmonic rejection was achieved by slightly detuning the two crystals from the parallel alignment. The energy resolution (FWHM) was 0.7 eV.

The XAFS spectra of the Ge K-edge were measured in transmission mode. Transmission spectra were recorded by two ionization chambers (N2, N2+He) with variable steps in the wave vector range 0.025 Å-1, count rate 2 s per point. The pre-edge positions were reproducible with a precision better than 0.01 eV.

Temperature dependence of EXAFS signals for Ge isotopes 70 and 76



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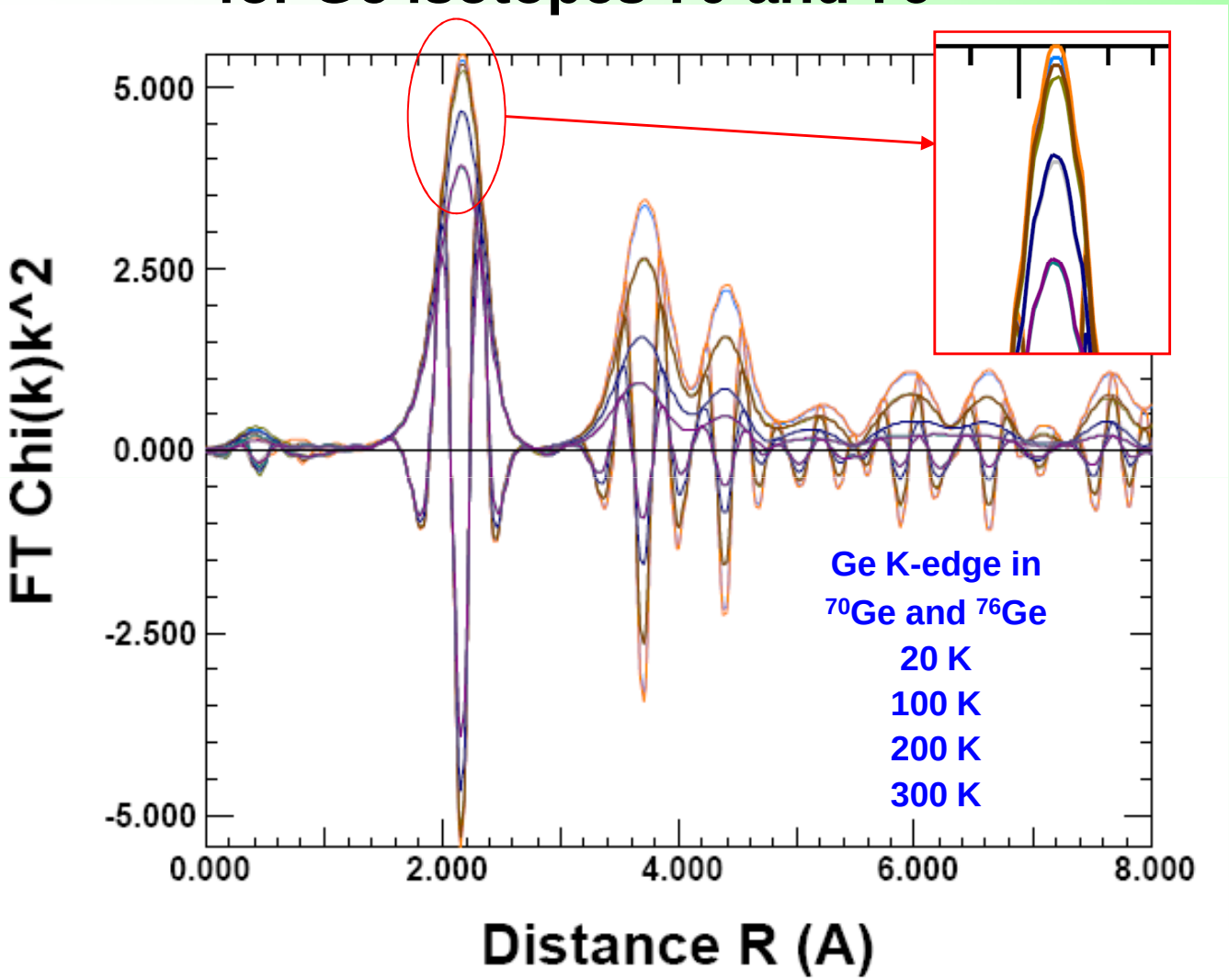
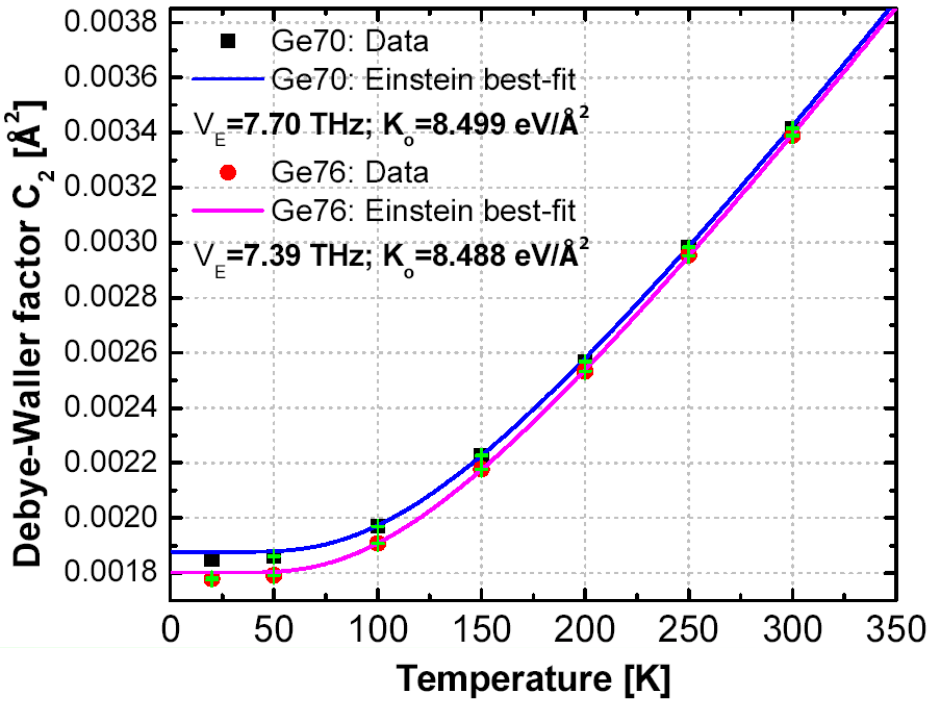
Temperature dependence of FT EXAFS signals for Ge isotopes 70 and 76

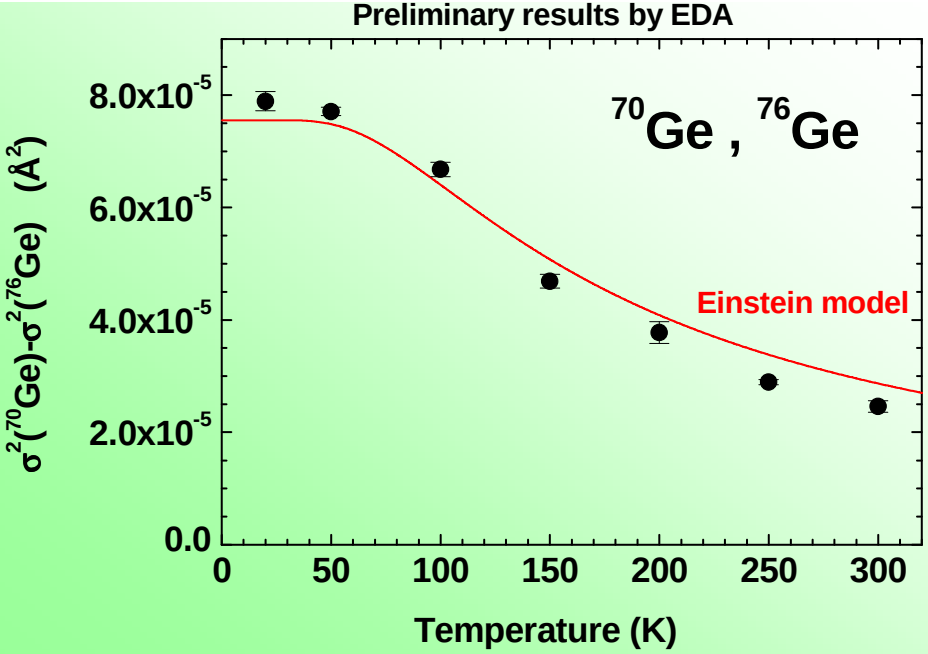


Difference between two Ge isotopes are visible at low temperatures.

Ge-Ge Debye-Waller temperature dependence in the first shell for Ge isotopes 70 and 76

Einstein model





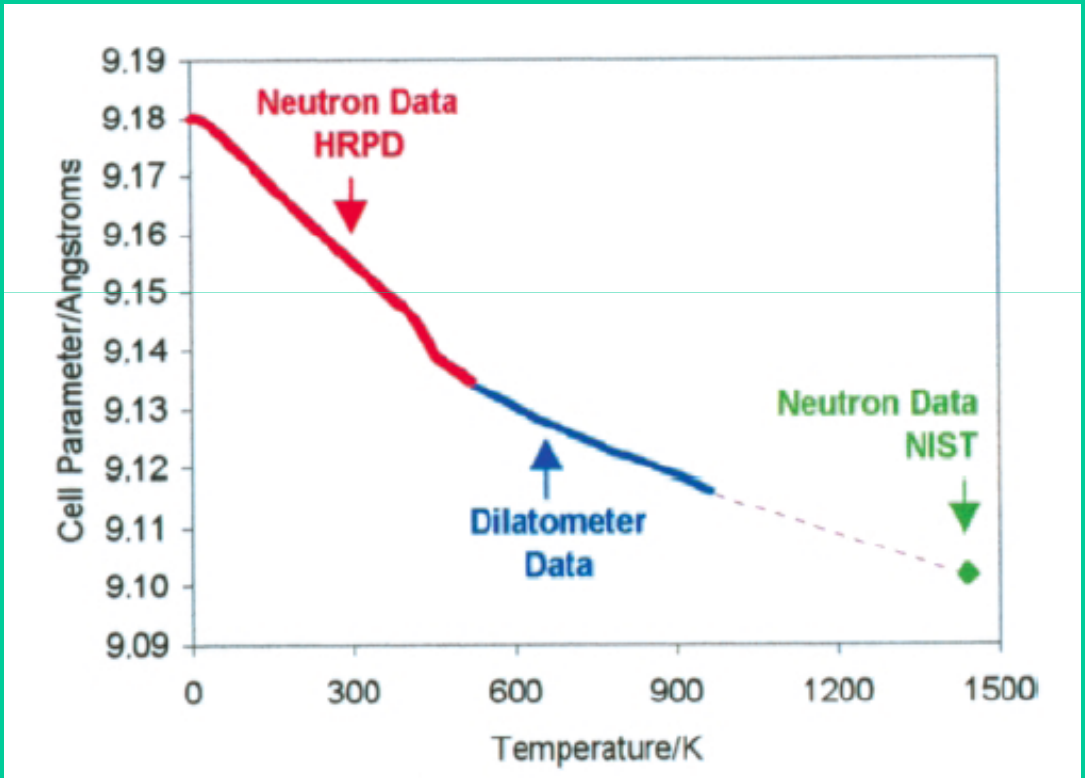
$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_BT}\right), \qquad (1)$$

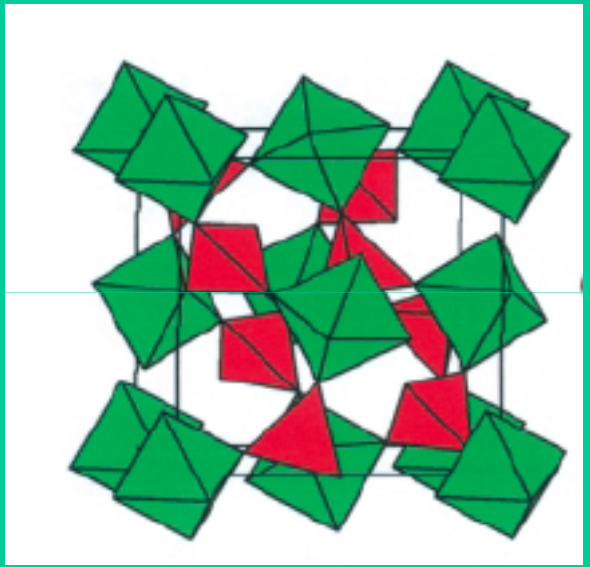
where the frequency ω_E is connected to an effective force constant k_0 through $\omega_E = \sqrt{k_0/\mu}$; μ is the reduced mass and k_B the Boltzmann constant. Since the force constant k_0 is expected not to depend on the isotopic composition, it is convenient to express the Einstein model in terms of only k_0 and μ. For $T \to 0$, $\sigma^2 \to \sigma_0^2 = \hbar/2\sqrt{\mu k_0}$, dependent on the isotopic composition. For $T \to \infty$, $\sigma^2 \to \sigma_\infty^2 = k_BT/k_0$ (classical behavior, independent of μ). One thus expects the isotopic effect to influence the zero-point value of σ^2, and progressively disappear when temperature increases. The measurement of the parallel MSRD σ^2 by EXAFS is generally easier and more accurate than the measurement of the uncorrelated MSD $\langle u^2 \rangle$ by Bragg diffraction.

NTE in framework structures

ZrW_2O_8

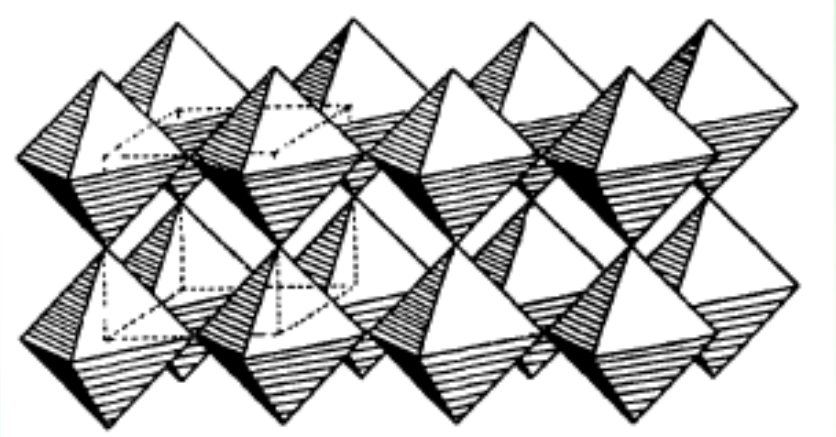
WO_4 + ZrO_6





Mary, Evans, Vogt, Sleight
Science, 272 (1996)

• ReO_3 has a cubic perovskite-type (ABO_3) structure composed of regular ReO_6 octahedra joined by vertices



•The $5d^1$ electronic configuration of Re^{6+} ions results in the partially filled conduction band, formed by the covalently mixed Re 5*d* and O 2*p* states and explaining the metallic conductivity of ReO_3. These conduction electrons play also the main role in the stabilization of the cubic structure of ReO_3.

• A number of phase transitions can be induced in ReO_3 by applying external pressure or by hydrogen insertion, that results in the formation of hydrogen rhenium bronzes H_xReO_3.

Table 1
Summary of RUM analysis for framework oxides

Structure families	Framework connectivity	Crystal symmetry	RUM	NTE
ReO_3 type	Pure octahedra corner-sharing network	C	Yes	No
AMO_5 types	Octahedra:tetrahedra = 1:1	T, O, M	Yes and no	Yes
$A_2M_3O_{12}$ types	Octahedra:tetrahedra = 2:3	R, O, M	No	Yes
ZrW_2O_8	Octahedra:tetrahedra = 1:2	C	Yes	Yes
ZrV_2O_7			No	
MO_2 types	Pure tetrahedra corner-sharing network	C, H, T, O	Yes	Yes

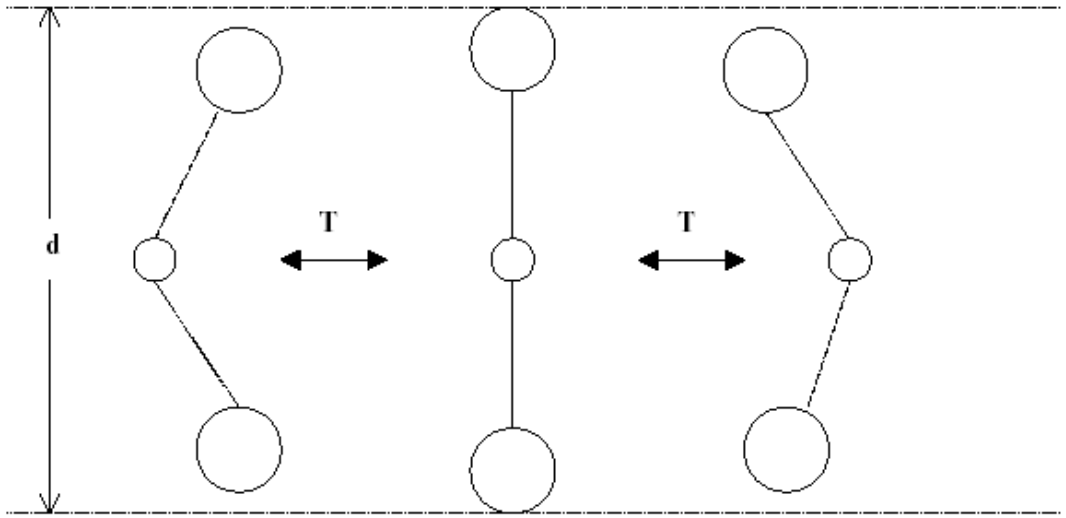
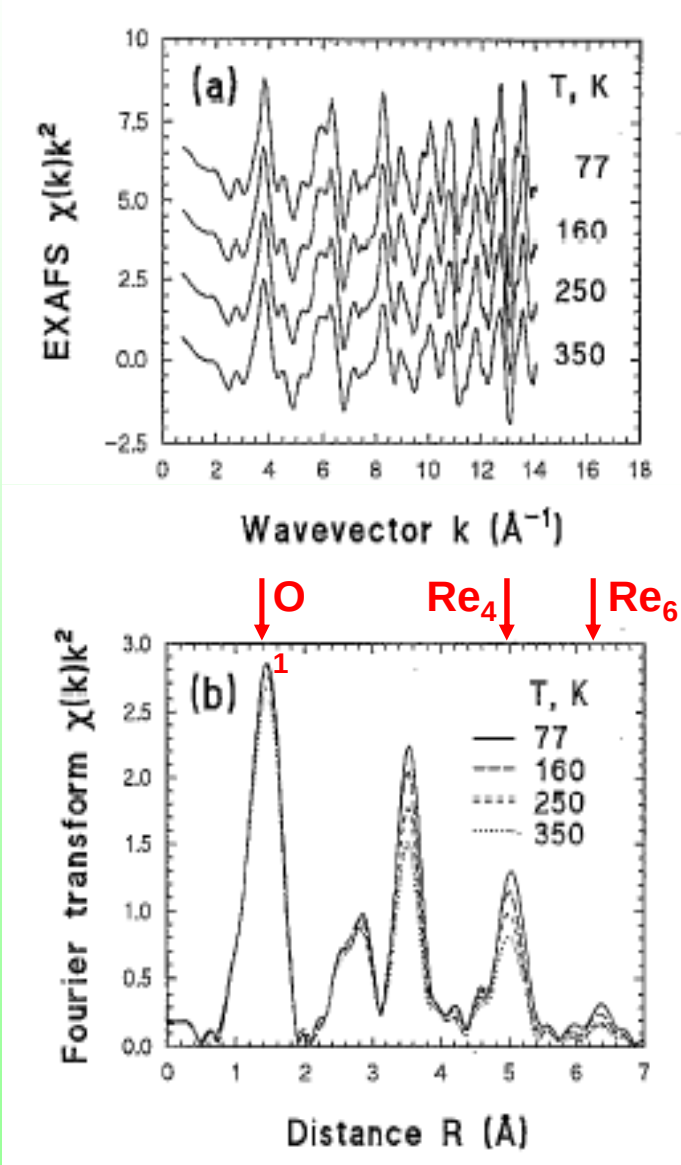
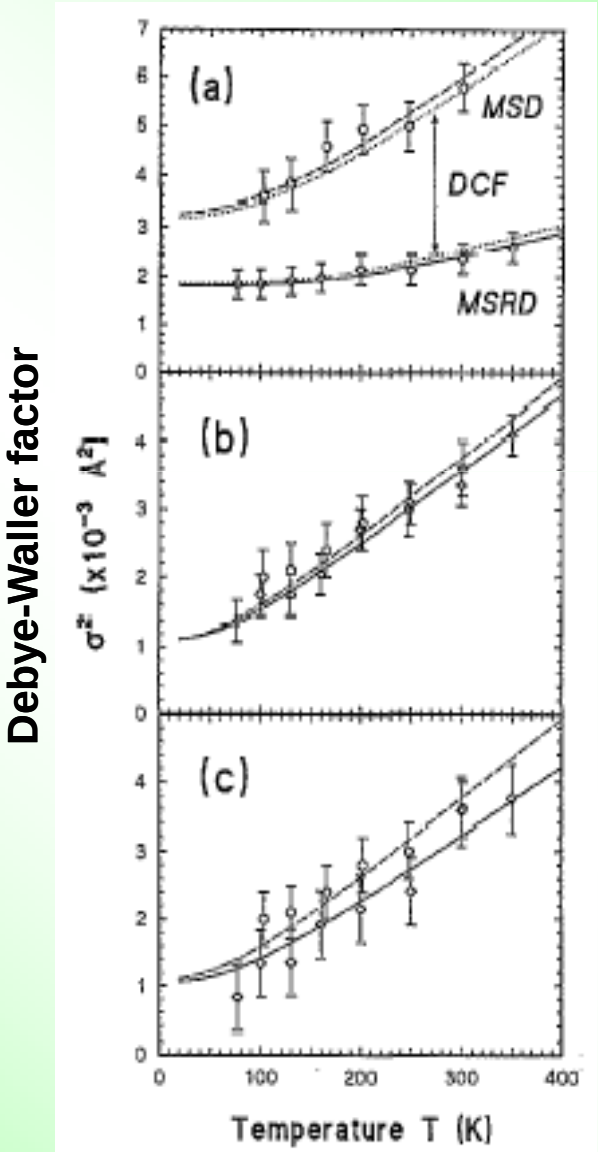


Fig. 8. Apparent decrease of interatomic distances due to thermal vibration of 2-coordinated oxygen atoms.

Temperature dependence of the EXAFS signals in perovskite-type ReO_3





Re_0-O_1

R=1.87 Å

Re_0Re_4

R=5.30 Å

Re_0-Re_6

R=6.49 Å

Temperature dependence of the EXAFS signals in perovskite-type ReO_3

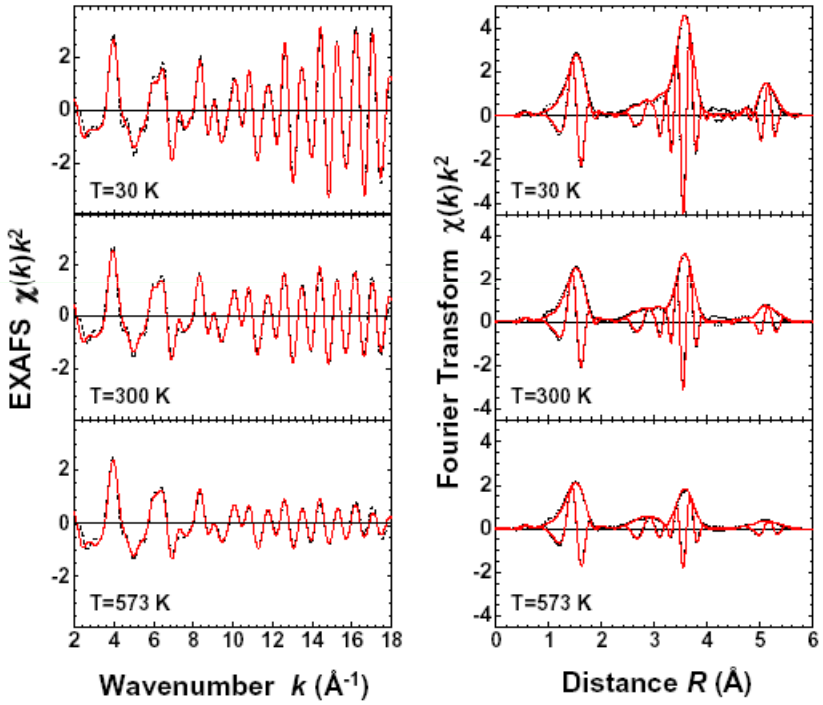
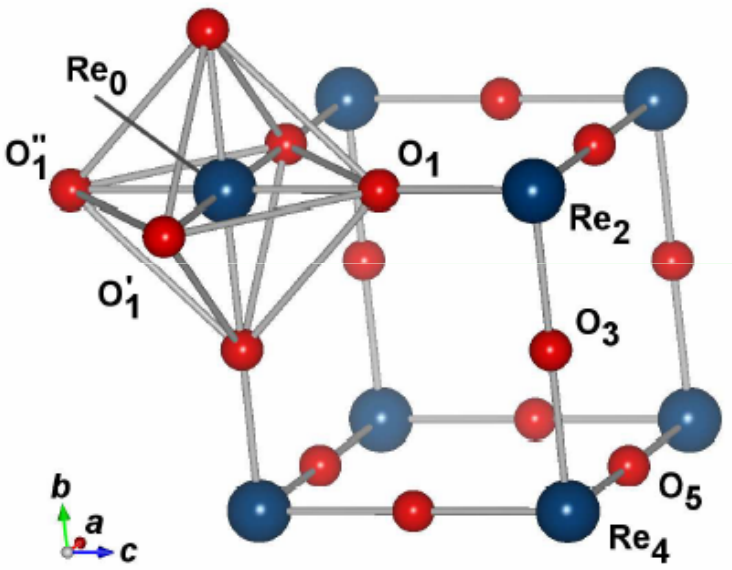


FIG. 4: (Color online) Best-fit results for the EXAFS $\chi(k)k^2$ signals (left) and the corresponding Fourier transforms (right) at three temperatures, obtained by the FEFFIT code. Dashed line - experiment, solid line - calculation. The fit was performed in the k-space interval $2-18$ Å^{-1}.



Summary and conclusions

- Our last experience at the beam-line BM-29 on ReO_3 and Ge shows that also *10* ***femtometer*** *(*10^{-4}Å) "barrier" is now attainable, even though such determination is far from trivial.

- Isotopic effects have been detected by EXAFS measurements on powdered samples of ^{70}Ge and ^{76}Ge. The most direct result is the high sensitivity to the difference of the amplitudes of nearest-neighbors relative vibrations (parallel MSRD), which has been measured with high accuracy from 20 to 300 K.

- The effect of isotopic mass has been revealed also in thermal expansion: the zero-point values of the nearest-neighbors average distance measured by EXAFS are consistent with the values ofdistance between average positions measured by Bragg diffraction.

Collaboration and Acknowledgments

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Thank You for attention !