P H Y S I C A L   R E V I E W   L E T T E R S

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

J. Purans,[1,2,*] N. D. Afify,[1] G. Dalba,[1] R. Grisenti,[1] S. De Panfilis,[3,4] A. Kuzmin,[2] V. I. Ozhogin,[5] F. Rocca,[6] A. Sanson,[6] S. I. Tiutiunnikov,[7] and P. Fornasini[1]

[1]*Dipartimento di Fisica, Università degli Studi di Trento, I-38050 Povo (Trento), Italy*
[2]*Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia*
[3]*Research Center Soft INFM-CNR, c/o Università di Roma La Sapienza, I-00185, Roma, Italy*
[4]*European Synchrotron Radiation Facility, Grenoble, France*
[5]*Institute of Molecular Physics, Russian Research Centre "Kurchatov Institute", 123182 Moscow, Russian Federation*
[6]*IFN-CNR, Istituto di Fotonica e Nanotecnologie, I-38050 Povo (Trento), Italy*
[7]*Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russian Federation*

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.

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The structural, electronic and dynamical properties of crystals are mainly dependent on the atomic number of the constituent atoms. The isotopic composition has subtle but non-negligible influence on some basic properties, like density, phonon widths, and electronic energy gaps [1]. Isotopic effects are relevant not only for their basic scientific interest, but also for several possible technological applications [2]. Of primary importance is the dependence of the dynamical properties of crystals on the isotopic composition [3]. The force constants depend on atomic species and crystal structure. The zero-point amplitude of atomic vibrations is however influenced also by the nuclear masses, the lighter isotopes undergoing larger oscillations than the heavier ones. As a consequence of anharmonicity, the difference in zero-point amplitude of motion reflects on a difference of interatomic equilibrium distances and lattice parameters [1]. These effects, of genuine quantum origin, progressively disappear when temperature increases.

The basic theory of the isotopic effect on lattice constants is well established [4]. The dependence of the lattice constants of diamond, silicon and germanium on isotopic composition has been theoretically evaluated in the quasi-harmonic approximation (QHA) using phonon frequencies calculated from first principles via density-functional perturbation theory [5]. Path-integral Monte Carlo simulations have been performed for germanium isotopes on the basis of a Stillinger-Weber potential and the results compared with the QHA approximation [6].

The low-temperature isotopic differences in lattice constant are usually proportional to the relative mass difference ($\simeq \Delta m/m$). In the case of germanium, the expected relative change in lattice parameter between ^{70}Ge and ^{76}Ge, according to the calculations of Ref. [5], is $\Delta a/a \simeq 5 \times 10^{-5}$. The difficulty in getting reliable experimental

results from conventional x-ray and neutron diffraction experiments [7] led to implement more sophisticated techniques. The difference in lattice constants of a ^{76}Ge thin film with respect to its supporting natural Ge single crystal has been measured from 54 to 300 K by x-ray standing waves [8]. The four highly enriched single-crystals isotopes ^{70}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge have been compared by x-ray backscattering in the temperature range 8–300 K [9,10]. The difference in thermal expansion between different isotopes of germanium has been checked also with ^{73}Ge nuclear magnetic resonance (NMR) [11].

Little attention has been up to now paid to the experimental detection of isotopic effects directly on the atomic mean square displacements. In this letter, we present an investigation of the isotopic effect in ^{70}Ge and ^{76}Ge performed by extended x-ray-absorption fine structure (EXAFS) spectroscopy. In an EXAFS experiment, the probes are the individual photoelectrons emitted by x-ray absorbing atoms and backscattered by neighboring atoms. Because of the photoelectrons short range, EXAFS can give original information on the local dynamics of crystals [12,13]. The sensitivity to the correlation of atomic motion makes EXAFS a complementary technique to diffraction, allowing one to measure the amplitude of relative vibrations as well as the thermal expansion of selected interatomic bonds. From the experimental point of view, EXAFS is particularly appealing for the possibility of using powdered samples, without the necessity of growing single crystals, and for the high accuracy attainable in the determination of atomic mean square relative displacements.

An EXAFS experiment samples a distribution of interatomic distances generated by thermal disorder. The distance distribution can be parametrized, to first order, in terms of its average value $\langle r \rangle$ and variance σ^2.

The variance σ^2, the so-called EXAFS Debye-Waller exponent, corresponds to the parallel mean square relative displacement (MSRD) $\langle \Delta u_\parallel^2 \rangle$, which is the sum of the uncorrelated mean square displacements (MSD) $\langle u^2 \rangle$ of absorber and backscatterer atoms along the bond direction, minus a displacement correlation function (DCF) [12]. The temperature dependence of σ^2 is the sum of the contributions of all normal modes [14]. It can, however, be satisfactorily reproduced by a simple Einstein model

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

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.

The average interatomic distance $\langle r \rangle = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$ measured by EXAFS is different from the distance between average atomic positions $R_c = |\langle \mathbf{r}_2 \rangle - \langle \mathbf{r}_1 \rangle|$, which is proportional to the lattice parameter a measured by Bragg diffraction. The difference between $\langle r \rangle$ and R_c is due to the effect of the perpendicular MSRD $\langle \Delta u_\perp^2 \rangle$ [13,14]:

$$\langle r \rangle = R_c + \langle \Delta u_\perp^2 \rangle / 2R_c. \qquad (2)$$

The perpendicular MSRD increases with temperature, and the thermal expansion measured by EXAFS is larger than the thermal expansion measured by Bragg diffraction [13,15]. According to Eq. (2), the isotopic effect on distances is expected to be larger in EXAFS than in Bragg diffraction. 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 $\simeq 10^{-3}$ Å [13,15] and in some cases $\simeq 10^{-4}$ Å [16]) 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 [17].

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 in the present work. Their room temperature Raman spectra are

in excellent agreement with that of Ref. [18]. EXAFS measurements have been done at the beam line BM29 of ESRF (Grenoble, France) [19]. Storage ring energy and average current were 6.0 GeV and 200 mA, respectively. Both germanium isotopes were finely ground by hand for a short time, and the resulting powders were then suspended in alcohol by a sonication technique. After sonication, only the lightest particles remained suspended in the fluid, and were deposited on polytetrafluoroethylene membranes. This well tested procedure gives very homogeneous samples, as required for experiments like the present one. The thickness of the sample was about 11 μm, optimized for obtaining a jump $\Delta(\mu x) \simeq 1$ at the Ge K absorption edge.

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 two crystals from the parallel alignment. The spectra were recorded by two ionization chambers filled with a mixture of argon and helium gases, with a count rate of 2 seconds per point. The preedge and edge regions were sampled at constant energy steps, $\Delta E = 5$ and 0.5 eV, respectively, whereas the EXAFS region was sampled at constant photoelectron wave number steps $\Delta k = 0.026$ Å^{-1}.

The sample's temperature was varied from 20 to 300 K at 50 K steps using a helium gas flow cryostat, and stabilized to better than 0.1 K. A sample of amorphous Ge at room temperature was placed after the second ionization chamber and its absorption was measured by means of a third ionization chamber in order to give a constant energy reference. At least two spectra were recorded at each temperature for each sample, to allow an evaluation of experimental uncertainty.

The EXAFS spectra have been independently analyzed using two different methodologies, supported by two different software packages, EXTRA [13] and EDA [20]. In both cases, the EXAFS signals were extracted according to well assessed procedures, and particular care was taken in the accurate relative alignment of the edges of all spectra. The first-shell contribution was singled out by Fourier filtering. Selected Fourier transforms (FT) are shown in Fig. 1, upper panel, up to the third coordination shell. The difference in the first-shell contribution to the magnitude of FT of the two isotopes at 20 K (lower panel of Fig. 1) is reproducible for all pair of compared files and different FT parameters utilized.

In the first step of the quantitative analysis of the first-shell contribution, the two isotopes have been separately considered, taking the 20 K spectra as reference: the results are the temperature dependencies of average distance $\langle r \rangle$, third cumulant (measuring the asymmetry of the distance distribution) and Debye-Waller exponent σ^2 of the two isotopes. In a second step, a comparison has been made of the two isotopes at each temperature: the results are the
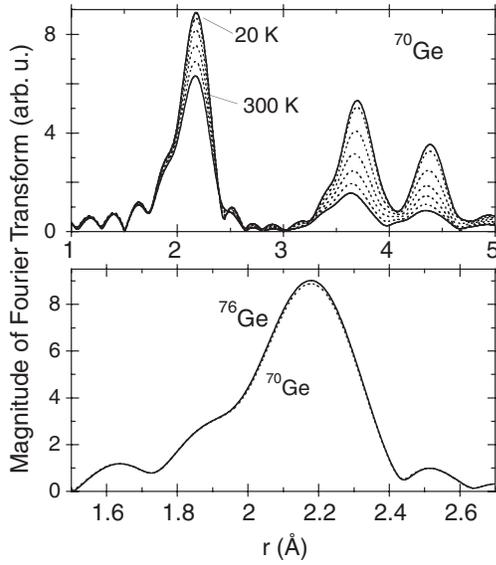
FIG. 1.   Modulus of Fourier transforms for ^{70}Ge at 20, 50, 100, 150, 200, 250, 300 K (from top to bottom in the upper panel) and comparison between the first-shell peak in the Fourier transforms of ^{76}Ge (solid line) and ^{70}Ge (dotted line) at 20 K.

differences in interatomic distances and Debye-Waller exponents between the two isotopes as a function of temperature; the difference of third cumulants was negligible. In the EXTRA procedure, phases and amplitudes have been separately analyzed by the *ratio method* [13]. In the EDA procedure [20], the values of distance and Debye-Waller exponent have been obtained by a nonlinear fit to the filtered 1st-shell spectra; the use of backscattering amplitudes and phase shifts taken from experiment guaranteed the same level of accuracy as for the EXTRA procedure. 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. A very good agreement was found between the results of the two procedures.

Let us first consider the Debye-Waller exponents σ^2 of the two isotopes separately (Fig. 2, upper panel). Absolute values (squares and circles) have been obtained by fitting Einstein models [13] to the experimental temperature dependence of both samples. At high temperatures, the Einstein models, as expected, asymptotically tend to the classical linear behavior, independent of mass. At low temperatures, the isotopic effect is very clearly evidenced.

The results of the Debye-Waller analysis are summarized in Table I. As expected, the frequency $\nu_E = \omega_E/2\pi$ decreases when the mass number increases. The force constants $k_0 = \mu\omega^2$, calculated from the masses and the measured frequencies, are, however, the same, quantitatively supporting the evidence of a genuine isotopic effect. The zero-point values of experimental data and Einstein models, $\sigma_0^2 = \hbar/2\sqrt{\mu k_0}$, are slightly different. The ratio $\sigma_0^2(70)/\sigma_0^2(76)$ is 1.038 and 1.042 for experimental data
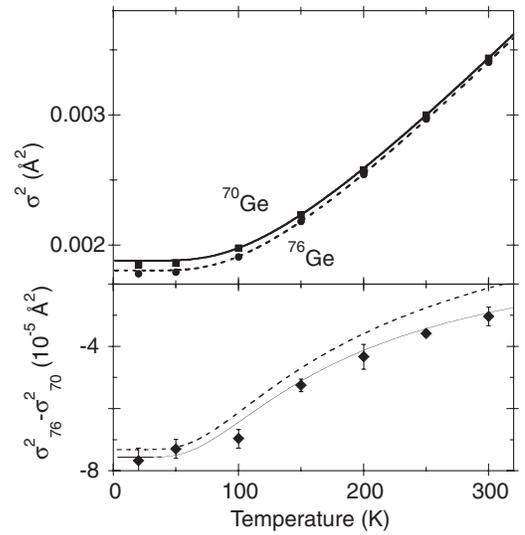
FIG. 2.   *Upper panel:* EXAFS Debye-Waller exponents σ^2 as a function of temperature for the two isotopes ^{70}Ge (squares) and ^{76}Ge (circles). The lines, solid and dotted for ^{70}Ge and ^{76}Ge, respectively, are the best fitting Einstein models. *Lower panel:* Difference of the Debye-Waller exponents of the two isotopes (diamonds); the solid and dashed lines are the differences between two Einstein models with the same (solid) and different (dashed line) values of the k_0 constant.

and Einstein models, respectively, in good agreement with the expected value $(76/70)^{1/2} = 1.042$.

The difference in the Debye-Waller exponents $\Delta\sigma^2 = \sigma^2(^{76}\text{Ge}) - \sigma^2(^{70}\text{Ge})$, obtained from the direct comparison of the experimental data of the two isotopes at each temperature, is shown in the lower panel of Fig. 2 (diamonds). The solid line is the difference between the two Einstein models with the same force constant k_0, determined from the separate analysis of the two isotopes (Table I); as expected, it goes asymptotically to zero when $T \to \infty$. The dashed line has been obtained by varying the force constant k_0 of one of the two Einstein models by 0.25%; at high temperatures it becomes positive. The agreement of the experimental points with the solid line and the discrepancy with the dashed line is a measure of the high sensitivity of the EXAFS Debye-Waller exponent to the isotopic effect.

TABLE I.   Comparison between ^{70}Ge and ^{76}Ge: atomic masses, zero-point values of experimental Debye-Waller exponents and best fitting Einstein models, Einstein frequencies ν_E and corresponding force constants k_0 of the nearest neighbors distance.

Atom	Mass	σ_0^2 (exp.)	σ_0^2 (Ein.)	ν_E	k_0
	(amu)	(10^{-3} Å^2)	(10^{-3} Å^2)	(THz)	(eV/Å^2)
^{70}Ge	69.92	1.849(1)	1.882(1)	7.70(2)	8.496(40)
^{76}Ge	75.92	1.782(1)	1.815(1)	7.39(2)	8.496(40)
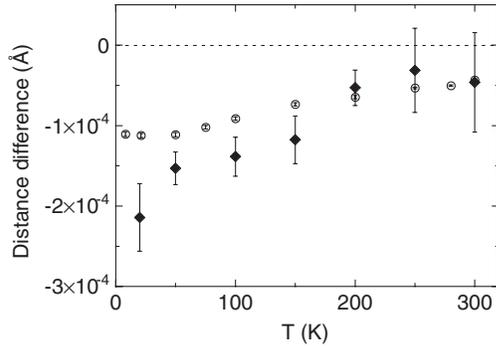
FIG. 3. Difference of the nearest-neighbors average interatomic distance in ^{76}Ge and ^{70}Ge, determined from EXAFS analysis (diamonds), compared with the difference of distance between average positions determined from x-ray backscattering [9] (open circles, containing the error bars).

The difference in average nearest-neighbors distances $\langle r(^{76}\text{Ge})\rangle - \langle r(^{70}\text{Ge})\rangle$, obtained from the direct comparison of the EXAFS phases of the two isotopes at each temperature, is shown by diamonds in Fig. 3. For comparison, the difference in distances between average positions $R_c(^{76}\text{Ge}) - R_c(^{70}\text{Ge})$, calculated from the x-ray backscattering results of [9], is shown as open circles. The difference between EXAFS and Bragg diffraction values is due to the effect of perpendicular atomic vibrations, Eq. (2). The low-temperature value of the ratio between perpendicular and parallel MSRD of germanium, experimentally determined in a previous work [15] and recently reproduced by *ab initio* calculations [21], is about 3.5. Accordingly, the difference of about 7.5×10^{-5} Å^2 directly measured for the parallel MSRD at 20 K (Fig. 2, lower panel) corresponds to a difference of about 2.6×10^{-4} Å^2 in the perpendicular MSRDs of the two isotopes, and, by (2), to a low-temperature difference between the isotopic effect on distances measured by EXAFS and by Bragg diffraction of about 0.53×10^{-4} Å. This value is consistent with the data shown in Fig. 3.

In conclusion, 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 of distance between average positions measured by Bragg diffraction. The possibility of detecting relative distance variations smaller than 10 femtometers by means of a conventional transmission EXAFS apparatus and a standard procedure of data analysis has been demonstrated.

*Corresponding author.
purans@cfi.lu.lv
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