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Nuclear forward scattering by the 68.7 keV state of ^{73}Ge in CaGeO$_3$ and GeO$_2$

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Abstract – We measured nuclear forward scattering of synchrotron radiation by the 68.7 keV nuclear resonance of ^{73}Ge with a half-life $T_{\frac{1}{2}} = 1.74$ ns. The Debye temperatures of CaGeO$_3$ in the wollastonite, garnet and perovskite phases were determined to be 386(20) K, 437(20) K and 507(20) K, respectively, and 309(20) K and 459(11) K for GeO$_2$ in the quartz and rutile phases, respectively. The isomer shift is clearly dependent on the Ge valence but not directly on the coordination geometry. The so far unknown magnetic moment μ_e of the 68.7 keV excited state of ^{73}Ge is determined to be $-0.84(22)\,\mu_\mathrm{N}$. Time domain ^{73}Ge Mössbauer spectroscopy with the 68.7 keV resonance is feasible for isomer shift and Debye temperature measurements but so far neither electric quadrupole nor magnetic hyperfine interactions could be observed.

Introduction. – Two excited nuclear states of the ^{73}Ge isotope at 13.2845(15) and 68.752(7) keV with half-lives $T_{\frac{1}{2}} = 2.92(3)\,\mu$s and $T_{\frac{1}{2}} = 1.74(13)$ ns, respectively [1], are suitable for Mössbauer spectroscopy. The first observation of the Mössbauer effect on the 68.7 keV state by Czjzek *et al.* [2] dates back to 1966. Coulomb excitation was used to populate the excited state. Czjzek *et al.* [3] and Zimmermann *et al.* [4] conducted the first Mössbauer experiments on the 68.7 keV state in Ge and GeO$_2$ in the rutile and quartz phases in 1968. In 1974, Raghavan and Pfeiffer [5] were the first to observe the Mössbauer effect on the 13.3 keV state of ^{73}Ge with a ^{73}As source. Ge Mössbauer spectroscopy (MS) is undoubtedly a valuable technique to study the chemistry and physics of Ge in a variety of material systems, *e.g.* in Ge bearing semiconductor devices for the investigation of defects [6] or in phase change materials where the Ge coordination is still a matter of debate [7,8]. The applicability of ^{73}Ge MS to the study of solid-state physics is, however, limited due to severe experimental difficulties [3–5,9]. For the 68.7 keV transition a Coulomb-excited source is necessary and the 13.3 keV transition exhibits a

high internal conversion factor and large electronic absorption cross-section due to K-edge absorption at 11.1 keV in close proximity to the transition energy resulting in a small cross-section for the γ-rays. Alternatively, synchrotron radiation can be used to populate the excited states of Mössbauer isotopes. Recently, Seto *et al.* applied synchrotron radiation-based MS to the 68.7 keV state of ^{73}Ge using GeO$_2$ quartz (96.4% ^{73}Ge enriched) as a reference absorber to record an energy domain spectrum of Li$_2$GeO$_3$ (natural ^{73}Ge abundance) with a total acquisition time of ~ 90 h [10].

Here we report on the application of nuclear forward scattering (NFS) [11] to the ^{73}Ge 68.7 keV Mössbauer transition. The experimental setup includes a ~ 24 meV energy bandwidth monochromator and a multielement detector. We investigated two model systems, CaGeO$_3$ and GeO$_2$, with distinct structural environments of tetravalent Ge in four-, mixed four/six- and six-fold Ge coordination. In addition, we studied GeS and GeSe with divalent Ge and pure Ge. These samples are ideal to study the influence of chemical bonding on the isomer shift. The lattice dynamics were studied by the determination of the
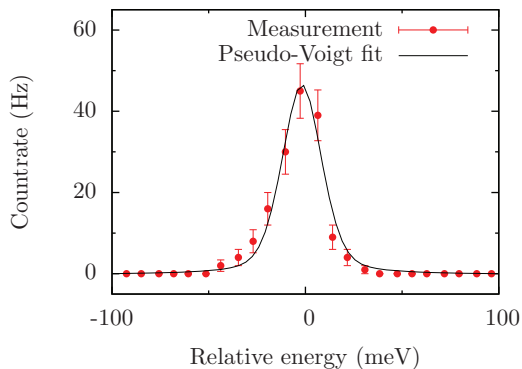
Fig. 1: (Colour on-line) The instrumental function, measured with $^{73}GeO_2$ rutile. The line represents a fit with a pseudo-Voigt function with 24(1) meV FWHM.

Lamb-Mössbauer factor and the Debye temperature. The GeO_2 measurements allowed us to validate the results obtained by MS [3,4]. We performed measurements with an applied magnetic field in order to determine the so far unknown nuclear magnetic moment μ_e of the ^{73}Ge excited state.

Experimental setup. – The experiment was performed at the nuclear resonance beamline ID18 at the European Synchrotron Radiation Facility. The storage ring was operated in the 16 bunch filling mode with a time window of 176 ns and an average beam current of 70 mA. The 68.7 keV incident radiation was monochromatized in two steps by a high-heat-load monochromator with Si (111) reflections followed by a medium-resolution monochromator composed of two pairs of Si (444) and Si (844) reflections arranged in a nested configuration [11]. The optical design of the reflections is similar to the one in ref. [12]. In order to improve the throughput of the monochromators the radiation was collimated by compound refractive lenses installed before the high-heat-load monochromator. The instrumental function, measured with $^{73}GeO_2$ rutile, has pseudo-Voigt shape with an energy bandwidth of 24(1) meV FWHM (fig. 1). The radiation scattered by the sample in forward direction was measured using a 16-element array of Si avalanche photodiodes which allows the separation in time of the electronic scattering from the nuclear resonant scattering and has $\sim 10\%$ efficiency, less than 0.02 Hz electronic noise and ~ 0.5 ns time resolution. The acquisition time per spectrum was ~ 1–2 h. The samples were placed in a cryomagnetic system with 3 K base temperature.

Sample preparation. – All investigated samples except for the two GeO_2 samples and Ge have natural isotopic abundance of 7.73% ^{73}Ge. $CaGeO_3$ wollastonite was synthesized by calcinating a stochiometric mixture of $CaCO_3$ and GeO_2 (quartz) at a temperature of 1200 °C for 6 h. The garnet phase of $CaGeO_3$ was synthesized from the wollastonite phase in a piston cylinder press at 1000 °C and a pressure of 3 GPa for 2 h. The $CaGeO_3$ garnet was then used a starting material for the synthesis of the $CaGeO_3$ perovskite which was conducted in a multianvil press at 1100 °C and 10 GPa for 2 h. Enriched $^{73}GeO_2$ in the rutile phase was hydrothermally synthesized from quartz-type $^{73}GeO_2$, 95.6 % ^{73}Ge enriched, at 600 °C and 0.1 GPa for 7 days. GeS powder was purchased from Sigma Aldrich. GeSe was synthesized from a stochiometric mixture of Ge and Se in Ar atmosphere at 1000 °C for 7 h. Ge, 95.6% ^{73}Ge enriched, was purchased from Chemgas. All samples were polycrystalline and phase purity was confirmed by X-ray powder diffraction.

Experimental method. – The time-dependent NFS signal is determined by hyperfine interactions, multiple scattering effects and the nuclear spins of the ground and excited state. The 68.7 keV state of ^{73}Ge has a nuclear spin of $I_e = 7/2$ and the ground state a spin of $I_g = 9/2$. The hyperfine interactions lift the degeneracy of the ground and excited nuclear states. This causes a periodic modulation of the NFS signal with frequencies proportional to the strength of the hyperfine interaction. Multiple scattering within the sample also leads to a time modulation with a frequency dependent on the thickness of the sample L, the Lamb-Mössbauer factor f_{LM} and the lifetime τ_0 of the excited state. f_{LM} is the recoil-free emission and absorption probability of γ-radiation by a nucleus. All NFS spectra of single compounds measured herein can be described solely by multiple scattering through a single-line absorber, *i.e.* without measurable hyperfine splitting. The time dependence of the spectra is then simply given by [13]

$$I(t,\xi) = \frac{I_0}{\Delta\omega} e^{-\mu_{el}L} \left(\frac{\xi}{\tau_0 t}\right)^2 e^{\frac{-(1+q)t}{\tau_0}} J_1^2 \left(2\sqrt{\frac{\xi t}{\tau_0}}\right), \quad (1)$$

where I_0 is the initial intensity in the frequency band $\Delta\omega$ determined by the monochromator, μ_{el} is the electronic absorption length, L is the sample thickness, $J_1(x)$ is the first-order Bessel function, $q > 0$ accounts for line broadening such as caused by a distribution of spectral parameters, which leads to a faster decay, and ξ is the effective thickness,

$$\xi = \frac{1}{4} L \frac{\beta}{V_{Ge}} \sigma_0 f_{LM}. \quad (2)$$

β is the isotopic enrichment factor, V_{Ge} is the volume per Ge atom and σ_0 is the nuclear resonant absorption cross-section. In order to account for inhomogenities in the sample thickness a distribution with five supporting points was used. The multiple scattering is nicely demonstrated in the case of GeO_2 rutile (fig. 2). The exponential decay due to the lifetime of the excited state is modulated by dynamical beats. With increasing temperature the beating period increases due to the decrease of f_{LM} (see fig. 3) and the beats are smeared out due to thickness inhomogenities within the sample. We use a Levenberg-Marquardt algorithm to fit eq. (1) to the NFS spectra. In addition, we use the MOTIF code [14] for the analysis of magnetic hyperfine interactions and isomer shifts.
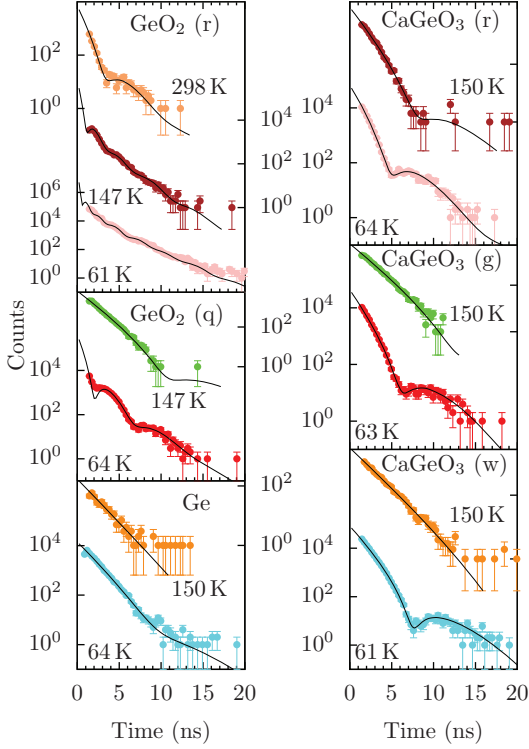
Fig. 2: (Colour on-line) The NFS spectra of ^{73}GeO$_2$ quartz and rutile, CaGeO$_3$ wollastonite, garnet and perovskite and pure ^{73}Ge between ~ 60 K and ~ 298 K. The lines are the fit to the data.

Fig. 3: (Colour on-line) $f_{LM}(T)$ (filled symbols) in CaGeO$_3$ garnet, perovskite and wollastonite, ^{73}GeO$_2$ quartz and rutile and ^{73}Ge obtained from the effective thickness $\xi(T)$. The lines are the fits according to the Debye approximation [17]. Open symbols correspond to MS results [3,4] and XRD results [18–22].

Results and discussion. –

Samples and spectra. We measured the NFS signal in CaGeO$_3$ garnet, perovskite and wollastonite, in ^{73}GeO$_2$ quartz and rutile and in ^{73}Ge between ~ 60 K and 298 K. These compounds exhibit different coordination numbers for Ge, are non-magnetic and in case of GeO$_2$ show an electric-field gradient on the Ge site as determined by NMR [15]. Ge crystallizes in the space group $Fd\bar{3}m$ with one Ge site that has cubic symmetry. The Mössbauer spectrum of Ge at 80 K does not show any hyperfine interactions and can be described as a single-line absorber [4]. We therefore expect the NFS spectrum to exhibit only dynamical scattering according to eq. (1). GeO$_2$ quartz crystallizes in the trigonal crystal system with Ge tetrahedrally coordinated by O. The Ge nuclei on this site are subject to an electric-field gradient (EFG) resulting in a quadrupolar coupling constant $C_Q = 9.2(5)$ MHz [15]. GeO$_2$ rutile adopts the tetragonal crystal structure with Ge six-fold coordinated by a distorted O octahedron. ^{73}Ge solid-state NMR revealed a quadrupolar coupling constant $C_Q = 19.3(5)$ MHz [15]. MS, however, revealed no observable hyperfine interactions and single-line spectra [3,4] for both GeO$_2$ phases. We thus expect the NFS spectra of both phases to obey eq. (1) with a possible line broadening $q > 0$ due to the EFG which should be larger for the rutile than for the quartz phase. The Lamb-Mössbauer factor and Debye temperature should also be larger than

for the quartz phase because the high-pressure rutile phase exhibits a smaller V_{Ge} and a more rigid lattice.

In the triclinic CaGeO$_3$ wollastonite Ge is tetrahedrally coordinated by O. The hyperfine parameters of ^{73}Ge in this compound are so far unknown. We attempt to describe the NFS spectrum by eq. (1) with a possible line broadening q. CaGeO$_3$ garnet adopts a tetragonal crystal structure where Ge occupies four- and six-fold O coordinated sites. Thus, we expected the NFS spectra to consist of two absorption lines, either separated by a measurable isomer shift or described as one broad line with a value of $q > 0$. In orthorhombic CaGeO$_3$ perovskite Ge is six-fold coordinated by an O octahedron and we describe the NFS spectra similar to those of wollastonite. The Lamb-Mössbauer factor and Debye temperature of the wollastonite phase are expected to be the lowest of the three because it is the ambient pressure phase and exhibits the largest V_{Ge}, whereas they should be the highest for the high-pressure perovskite phase due to the smallest V_{Ge}. The NFS spectra and fits are shown in fig. 2.

Although there is an electric-field gradient present at the Ge site in GeO$_2$ quartz and rutile [15] no hyperfine interactions are observable, in line with MS results [3,4]. This can be related to a small nuclear quadrupole moment of the excited state. However, quadrupole hyperfine interactions might be observed in compounds with larger electric-field gradients, *e.g.* Ge-V layered compounds [16].

Table 1: The Debye temperatures θ_D obtained from the fit of the effective thickness $\xi(T)$.

	θ_D (K)	
	This work	[4,23]
$CaGeO_3$ (w)	386(20)	
$CaGeO_3$ (g)	437(20)	
$CaGeO_3$ (p)	507(20)	
$^{73}GeO_2$ (q)	309(20)	255(16)
$^{73}GeO_2$ (r)	459(11)	426(16)
^{73}Ge	399(20)	263(11), 374(2)

The $CaGeO_3$ garnet NFS spectra reveal also a single-line absorber which indicates that the difference in the Ge coordination between the two sites does not cause a measurable splitting of the absorption lines.

Lattice dynamics. In the Debye approximation, the Lamb-Mössbauer factor f_{LM} is a function of the temperature T and the Debye temperature Θ_D, see ref. [17]. As $\xi(T)$ is directly proportional to $f_{LM}(T)$, see eq. (2), $f_{LM}(T)$ and Θ_D are obtained by separating $\xi(T)$ into a temperature-independent and sample-dependent fit parameter $L\beta\sigma_0/(4V_{Ge})$ and the temperature-dependent $f_{LM}(T)$. Two data points are sufficient in the Debye approximation in order to determine these two fit parameters and thus Θ_D. We estimate the uncertainty to $\Delta\Theta_D = \pm 20$ K. With more than two data points the uncertainties can be directly obtained from the fit procedure. The results are shown in fig. 3 and table 1 together with MS results [3,4]. Among the $CaGeO_3$ phases the perovskite exhibits the highest Θ_D, whereas wollastonite exhibits the lowest, and this matches our expectations. The same relation is observed for the high-pressure rutile phase of GeO_2 which reveals a higher Θ_D than the quartz phase. f_{LM} can also be estimated from mean square displacements $\langle u^2 \rangle$ according to $f_{LM} = \exp(-k_\gamma^2 \langle u^2 \rangle)$ with the wave vector $k_\gamma = 34.9$ Å^{-1} using published XRD data [18–22] at room temperature, see fig. 3. The calculated values of f_{LM} at 78 K according to the Debye approximation agree well with the literature data for GeO_2 quartz and rutile [3,4]. The values obtained from room temperature XRD data are also in good agreement with our results. For Ge, however, our results deviate strongly from ref. [4], but agree with ref. [23]. The XRD data for the $CaGeO_3$ polymorphs give lower values for f_{LM} than the NFS measurements. These deviations are probably related to an overestimated $\langle u^2 \rangle$ in the refinement of the XRD data. With these high values of f_{LM} ^{73}Ge nuclear resonance scattering can be extended to nuclear inelastic scattering (NIS) for measurements of the density of phonon states (DPS) provided that a meV energy resolution monochromator can be designed, *e.g.* by using a sapphire backscattering monochromator [24].

Nuclear magnetic moment of the excited state. The nuclear magnetic moment μ_e of the 68.7 keV excited state of ^{73}Ge is unknown. In order to put a constraint on its
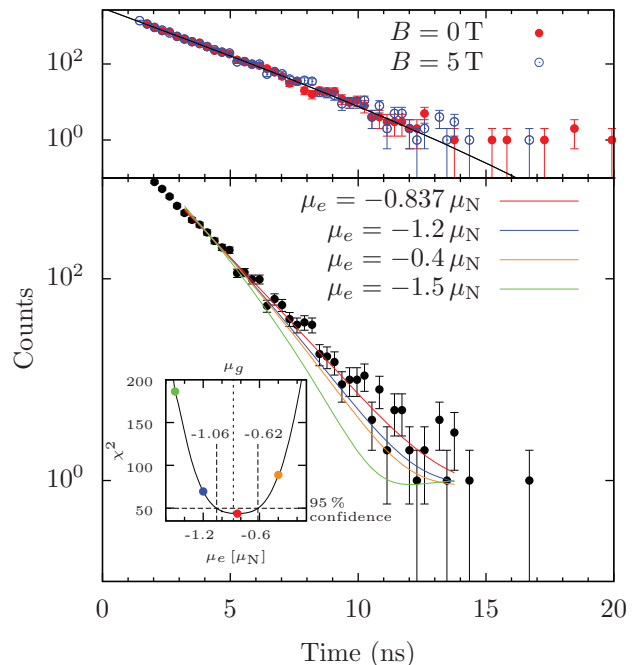

Fig. 4: (Colour on-line) Top: NFS for $CaGeO_3$ wollastonite at 150 K with and without an applied magnetic field of 5 T. Lines are the fits to the data, with eq. (1) and $\xi = 0.41(4)$. The two fits are not distinguishable. Bottom: NFS measured in $CaGeO_3$ wollastonite at 5 T and 150 K. The lines are modelled with different nuclear magnetic moments μ_e of the excited state. Inset: the goodness of the fit criterion χ^2 as a function of the nuclear magnetic moment μ_e of the excited state.

value the NFS was measured for diamagnetic $CaGeO_3$ in the wollastonite phase at 150 K in an applied magnetic field of 0 and 5 T, see fig. 4. The time spectra are essentially identical, which indicates that the magnetic moments of the excited and ground states must be similar. We can fit both spectra simultaneously according to eq. (1) with one set of parameters, which yields $\xi = 0.41(4)$ without taking any hyperfine interactions into account. As no hyperfine splitting is visible, a range can be determined for μ_e. We fitted the time spectrum for different values of μ_e under the assumption of randomly oriented nuclear spins in a magnetic field of 5 T. The nuclear magnetic moment of the ground state is $\mu_g = -0.878241(44)\,\mu_N$ [25]. The only free fit parameter is then a scaling factor. The best fit is obtained for $\mu_e = -0.84\,\mu_N$ with $\chi^2 = 43.6$ (fig. 4) and the number of degress of freedom, $n = 37$. At a 95 % confidence μ_e must lie in the range $-1.06\,\mu_N \leq \mu_e \leq -0.62\,\mu_N$. Larger hyperfine fields at the Ge nucleus might, however, be found in Fe-Ge alloys [26] or ErGe$_3$ [27].

Isomer shifts. In contrast to MS the determination of the isomer shift, δ, with NFS requires an additional second absorber as a reference compound. The NFS of a mixture of two compounds with different δ exhibits beats which arise from the interference of the corresponding absorption lines with a frequency dependent on the relative isomer shift [13]. The NFS time spectra of GeS and GeSe
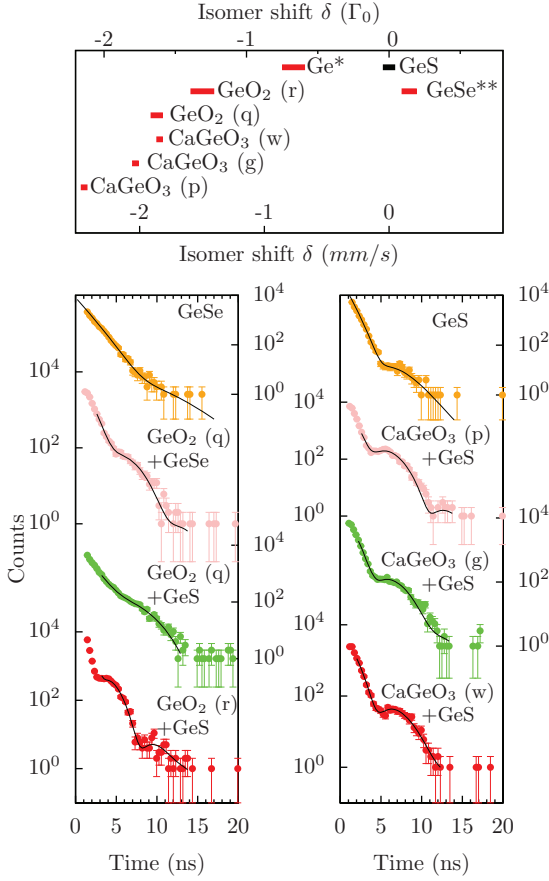
Fig. 5: (Colour on-line) Left: the NFS of mixtures of ^{73}GeO$_2$ quartz and rutile with GeS at 98 K and 298 K, respectively, of ^{73}GeO$_2$ quartz and GeSe at 15 K and of pure GeS and GeSe at 3 K. Right: the NFS of mixtures of the CaGeO$_3$ phases with GeS at 15 K. Lines are the fit to the data. Top: the isomer shifts with respect to GeS at 15 K. *Ge was calculated from our results and [3,4]; **GeSe from the GeO$_2$ vs. GeSe measurement.

Table 2: Isomer shifts δ of CaGeO$_3$ and ^{73}GeO$_2$ with respect to GeS and GeSe in units of the natural line width $\Gamma_0 = 1.14(9)$ mm/s at 15 K; *Ge was calculated from [3,4] and our results. δ of GeO$_2$ quartz and rutile and Ge were corrected for the second-order Doppler shift to 15 K.

	$\delta(\Gamma_0)$	Reference
^{73}GeO$_2$ rutile	$-1.31(8)$	GeS
^{73}GeO$_2$ quartz	$-1.63(4)$	
CaGeO$_3$ wollastonite	$-1.61(2)$	
CaGeO$_3$ garnet	$-1.78(2)$	
CaGeO$_3$ perovskite	$-2.14(2)$	
Ge*	$-0.67(8)$	
^{73}GeO$_2$ quartz	$-1.77(3)$	GeSe

indicates that our measured values for GeO$_2$ must have a negative sign and we can calculate $\delta^{GeS} = -0.67(8)\,\Gamma_0$ for Ge, where we corrected for the SOD to 15 K and used the conversion factor $1\Gamma_0 = 1.14(9)$ mm/s. We obtain $\delta = 0.32(9)\,\Gamma_0$ between GeO$_2$ quartz and rutile which is in agreement with [3,4]. ^{119}Sn MS shows the same order of δ for SnO$_2$, α-Sn and SnS [29–31]. In analogy to MS of CaSnO$_3$ we assume δ^{GeS} of the CaGeO$_3$ polymorphs to be negative [30]. Our measured δ^{GeSe} of GeO$_2$ quartz with respect to GeSe, $\delta^{GeSe} = -1.77(3)\,\Gamma_0$, must be negative [4] and is in good agreement with $\delta = -2.05(46)\,\Gamma_0$ in ref. [4]. Thus, for GeSe $\delta^{GeS} = 0.14(5)\,\Gamma_0$.

The isomer shift is a function of the electron density at the nucleus and accordingly the valence of Ge. In the GeO$_2$ and CaGeO$_3$ modifications ionic bonding of Ge(IV) is predominant. In GeS and GeSe, the Ge is divalent. As seen from fig. 5, values for Ge(II) and Ge(IV) compounds cluster together, which justifies our assumption of a negative isomer shift of the CaGeO$_3$ polymorphs with respect to GeS. The isomer shift is also a function of the structural environment. CaGeO$_3$ in wollastonite and GeO$_2$ in the quartz modification exhibit the same isomer shift. This is in line with the same Ge-O bond length in CaGeO$_3$ wollastonite and GeO$_2$ quartz [32,33] and with the common four-fold Ge coordination. The structural environment in these two compounds as seen by Ge K-edge EXAFS is also very similar [32]. In contrast, in CaGeO$_3$ perovskite and GeO$_2$ rutile we find significantly different isomer shifts despite the similar six-fold Ge coordination, a difference ascribed to the location of Ge in GeO$_2$ rutile in a distorted octahedron with four short and two long Ge-O bonds [33] whereas there are six Ge-O bonds of similar length in CaGeO$_3$ perovskite [18,34]. In CaGeO$_3$ garnet the Ge occupies two distinct crystallographic sites with a four- and six-fold coordination. We determined the isomer shift under the assumption of a single nuclear site because the NFS is consistent with a single-line absorber (fig. 2). Thus, clearly, δ is not governed unambiguously by the Ge coordination geometry. Considering the different Ge-O bond lengths and the volumes of the O octa- and tetrahedra surrounding the Ge we find no evidence for a

(fig. 5) both can be described through single-line absorbers according to eq. (1) and are consequently suitable reference compounds. In order to determine δ of CaGeO$_3$, in wollastonite, garnet and perovskite, and GeO$_2$, in quartz and rutile modifications, we measured the NFS of mixtures of those compounds with GeS and GeSe between 3 K and 298 K (fig. 5). For the fit of the time spectra we calculated f_{LM} of the compound under investigation from the obtained Debye temperature. f_{LM} of the reference compound —GeS or GeSe— and δ are free fit parameters. The results are shown in fig. 5 and table 2. δ of quartz and rutile GeO$_2$ vs. GeS measured at 98 K and 298 K, respectively, were corrected to 15 K for the second-order Doppler shift (SOD) [28] using the obtained Debye temperatures. NFS is sensitive to the modulus of δ. According to the weighted average of [3,4], the MS isomer shifts of GeO$_2$ quartz and rutile with respect to Ge are $-1.00(8)$ and $-0.88(8)$ mm/s, respectively. We assume that δ^{GeS} of both GeO$_2$ phases with respect to GeS have the same sign. δ^{GeS} of quartz must be smaller than δ^{GeS} of rutile which

correlation between the structure and δ. The separation of the CaGeO$_3$ and GeO$_2$ in δ indicates a significant influence of the presence of other cations, Ca(II), on δ.

Conclusion. – Nuclear forward scattering by the third excited nuclear state of ^{73}Ge with an energy of 68.7 keV was measured in a series of compounds and Lamb-Mössbauer factors and the Debye temperatures of Ge in CaGeO$_3$ garnet, perovskite and wollastonite, ^{73}Ge and ^{73}GeO$_2$ quartz and rutile were determined. Our results agree with the literature for Ge and GeO$_2$ quartz and rutile. Measurements of the isomer shift relative to GeS and GeSe revealed a clear dependence of the isomer shift on the Ge valence but no direct dependence of the isomer shift on the Ge coordination geometry. Neither quadrupole nor magnetic hyperfine interactions have been observed. The so far unknown magnetic moment μ_e of the excited state of ^{73}Ge is determined to be $\mu_e = -0.84(22)\,\mu_N$. Compared to conventional and synchrotron-radiation–based MS ^{73}Ge NFS is a faster experimental technique which can be easily applied even to samples with natural abundance of ^{73}Ge.

$* * *$

Note added in proofs: After the acceptance of the present paper ref. [35] was published in which the design of the optical reflections of the medium-resolution monochromator is described.

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