



	<b>Experiment title:</b> A Ge-73 nuclear forward scattering study of the Ge coordination in phase change materials	<b>Experiment number:</b> HS4633
<b>Beamline:</b> ID18	<b>Date of experiment:</b> from: 01.06.2013 to: 05.06.2013	<b>Date of report:</b> 01.03.2013
<b>Shifts:</b> 12	<b>Local contact(s):</b> Rudolf Rueffer	<i>Received at ESRF:</i>
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## Report:

During the beam time allocated for proposal HS 4633 nuclear forward scattering (NFS) by the 68.7 keV resonance ( $I=7/2 \rightarrow 9/2$ ) of  $^{73}\text{Ge}$  with a half life of  $t_{1/2}=1.74$  ns was performed in a series of Ge-compounds including thin film Ge-Sb-Te phase change materials.

The experimental setup consisted of a medium resolution monochromator leading to a 24(1) meV energy bandwidth, a 16 element detector array of silicon avalanche photodiodes, a KB x-ray focusing optic which was used for the thin film samples and a cryomagnetic system with 3K base temperature. An isotopically enriched  $^{73}\text{GeO}_2$  powder sample in the rutile phase was used to set the monochromator to the resonance energy of the excited state.

NFS time spectra were recorded for powder samples of  $\text{CaGeO}_3$  in the wollastonite, garnet and perovskite phases,  $^{73}\text{GeO}_2$  in the quartz and rutile phases, GeS and pure  $^{73}\text{Ge}$  at different temperatures. All NFS time spectra can be described solely by dynamical scattering through single line absorbers, i.e. without measurable hyperfine splitting. Representative NFS time spectra of  $\text{CaGeO}_3$  in the wollastonite, perovskite and garnet phases with tetrahedral (4-fold), octahedral (6-fold) and mixed (4+6-fold) Ge coordination, respectively, are shown in Figure 1 exhibiting dynamical beats. From the temperature dependent NFS time spectra it was possible to extract the Lamb-Mössbauer-factor  $f_{\text{LM}}$  and the Debye temperature  $\Theta_{\text{D}}$ , c.f. Figure 2. The Lamb-Mössbauer-factor  $f_{\text{LM}}$  of  $\text{GeO}_2$  in the rutile and quartz phases are in good agreement with the results from Zimmermann *et al.* [1] and Czjzek *et al.*[2].

The nuclear magnetic moment  $\mu_{\text{N}}$  of the 68.7 keV excited of  $^{73}\text{Ge}$  is unknown. In order to put a constraint on its value the NFS time spectrum of diamagnetic  $\text{CaGeO}_3$  in the wollastonite phase at 150 K in an applied magnetic field of 0 and 5 T was measured. The time spectra are essentially identical which indicates that the magnetic moment  $\mu_{\text{e}}$  of the excited state must be similar to that of the ground state  $\mu_{\text{g}}=-0.8792 \mu_{\text{N}}$ . Simulations of the NFS time spectra with different values for the magnetic moment of the excited state reveal that its values is strictly confined to  $-0.3 \mu_{\text{N}} < \mu_{\text{e}} < -1.4 \mu_{\text{N}}$ , see Figure 3.

The isomer shift  $|\delta|$  of  $\text{CaGeO}_3$  in the wollastonite, garnet and perovskite phases and of  $\text{GeO}_2$  in the quartz and rutile phases were determined relative to  $\text{GeS}$  as a reference compound, see Figure 4.

The following thin film phase change materials were investigated:  $^{73}\text{GeTe}$  and  $^{73}\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  in the amorphous and cubic phases and  $^{73}\text{GeSb}_2\text{Te}_4$  and  $^{73}\text{Ge}_2\text{Sb}_2\text{Te}_5$  in the amorphous, cubic and hexagonal phases. The film thicknesses were around 200 – 300 nm. The samples were inclined with respect to the beam direction in such a way that the beam was almost parallel to the film surface in order to achieve a reasonable effective thickness. The beam was focused to 30  $\mu\text{m}$  in vertical direction in order to avoid passing through the substrate and to increase the countrate. Due to the small film thickness it was difficult and time consuming to correctly position the samples and for a few samples it was not possible to record a NFS time spectrum. Thus, NFS measurements in phase-change materials could only be taken at one temperature. The spectra do not reveal any measurable hyperfine splitting.

In summary, NFS by the 68.7 keV resonance of  $^{73}\text{Ge}$  is not suitable to investigate hyperfine interactions because the nuclear magnetic moment of the excited state is very similar to that of the ground state and because even in standard samples with known electric field gradients at the Ge-site, e.g.  $\text{GeO}_2$  [3], no quadrupole splitting can be observed. However, the Lamb-Mössbauer-factor and the Debye temperature can be easily determined by recording the NFS time spectra at three different temperatures. The isomer shift of Ge relative to a reference compound, in this case  $\text{GeS}$ , can also be readily measured.

#### References:

- [1] Zimmermann *et al.*, Phys. Stat. Sol. (B), 27(2) (1968) 639.
- [2] Czjzek *et al.*, Phys. Rev. 174(2) (1968) 331
- [3] Michaelis *et al.*, J. Phys. Chem. C 114(49) (2010) 21736

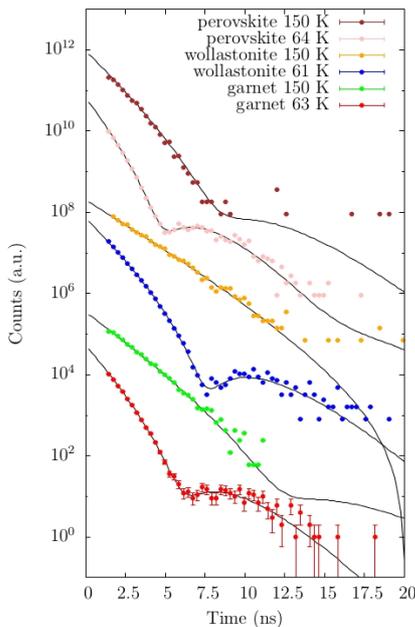


Fig. 1: NFS time spectra of  $\text{CaGeO}_3$  (wollastonite, garnet and perovskite) at different temperatures.

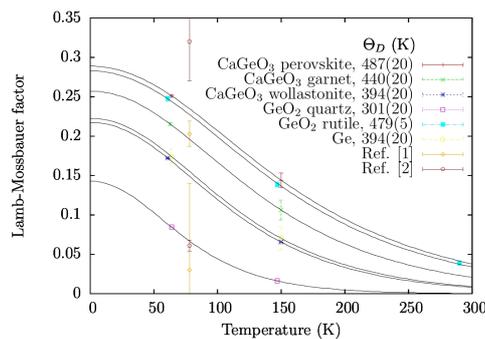


Fig. 2: Lamb-Mössbauer-factor as a function of temperature in the Debye approximation for several compounds. Results reported in [1] and [2] for both  $\text{GeO}_2$  phases are also shown.

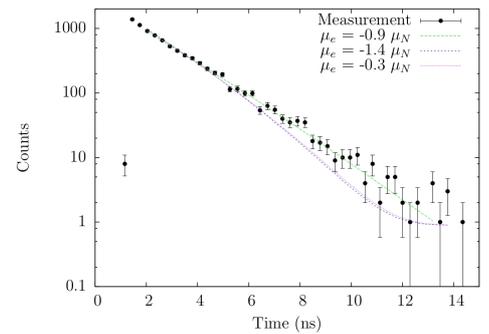


Fig. 3: Simulated NFS time spectra of  $\text{CaGeO}_3$  (wollastonite) at 150 K and an applied magnetic field of 5 T with different values of the nuclear magnetic moment of the excited state.

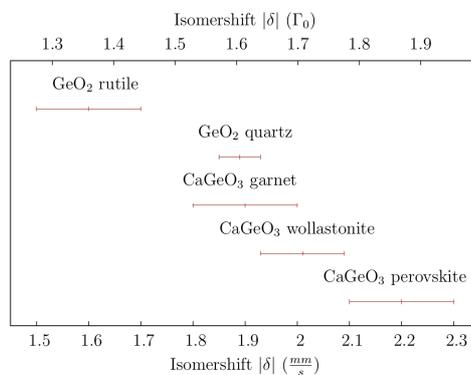


Fig. 4: Isomer shifts of several compounds measured relative to  $\text{GeS}$ .