Mass-selective neutron spectroscopy of glassy versus polycrystalline structures in binary mixtures of beryllium and zirconium

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Abstract. Exploiting the unique tandem of VESUVIO and TOSCA inverted geometry spectrometers at the ISIS pulsed neutron and muon source in the United Kingdom, specifically the capability of VESUVIO to measure concurrently neutron diffraction and Compton spectroscopy, we have performed a global study of the structural and dynamical origins of disorder in Zr—Be metallic glasses. To this end, a polycrystalline Zr30Be70 and an amorphous Zr40Be60 systems were investigated in a wide range of temperatures ranging from 10 to 300K. For the first time, neutron diffraction has provided clues as to the structural composition of the polycrystalline Zr30Be70. The Rietveld refinement of the diffraction data has revealed that the polycrystalline system is made up of three distinct structural phases; a hexagonal phase, Be2Zr, of the P6/mmm symmetry amounting to 87.11%, a second hexagonal phase, Be5Zr, of the P6/mmm point group symmetry, amounting to 12.89%, as well as trace amounts of a third orthorhombic phase of unspecified stoichiometry. The overall sample stoichiometry, inferred from the dissection of the diffraction data, was in excellent agreement with the Compton results, both confirming the Zr30Be70 formulation. The analysis of INS data agreed very well with the theoretical results from the recursion method. The INS data were cross-validated by the nuclear momentum distributions of both Zr and Be, obtained from the analysis of the NCS data. Systematic differences between the crystalline and amorphous Zr—Be systems were identified in the whole temperature range and attributed to low-frequency mode softening, when going from crystalline to the amorphous phase.

1. Introduction
Despite the intense interest in metallic glasses for a variety of engineering applications, many details of their structure and dynamics remain a mystery. One of the iconic pieces of this unsolved puzzle is due to their phonon-related properties. Metallic glasses are at least two-component systems. From the point of view of lattice dynamics, two-component periodic systems should exhibit acoustic and optic vibrational modes. An acoustic dispersion relation has been observed
in many metallic glasses [1, 2, 3, 4] by neutron and X-ray inelastic scattering methods. A model theoretically describing the dispersion relation of collective excitation in Mg_{70}Zn_{30} with a combination of acoustic and optic modes has been made by Hafner [5]. Otomo [3] suggested that collective excitations in Ni_{32}Zr_{67} originate from the combination of three ‘optical’ modes in the crystalline phase. Noticeably, in the same amorphous samples the dispersion of optical modes was not clearly observed.

Zr—Be amorphous alloys hold a special place among other metallic disordered systems. Because of the large difference in atom sizes and masses alloys can become amorphous in a wide range of compositions [6]. Zr—Be amorphous systems are also attractive in terms of industrial application. Physically vapor-deposited metallic Be has been used currently as a brazing filler metal [7]. ZrBe binary amorphous alloys were investigated as a new filler metal for joining zirconium alloy to supersede vapour-deposited beryllium [8].

One specific computational method of solid state physics is celebrated in the context of computational studies of metallic glasses, the recursion method [6]. The method relies on the presence of short-range order within a solid state matrix under investigation. In such case, the long-distance interactions can be neglected and the dynamical matrix of the whole system can be greatly reduced in dimensionality to a handful of force constants between neighbours and next-neighbours [9, 10]. Mathematically, the phonon modes are usually calculated in this method by tri-diagonalizing the dynamical matrix describing the forces in a basis of orthonormal operators [9]. It is the application of the recursion method to the calculation of generalised vibrational density of states (GVDOS) and atom-projected vibrational density of states (apVDOS) in amorphous Zr_{1-x}Be_{x} systems with (x = 0.3 - 0.5) which is at the centre of the experimental and computational work by Bratkovskyy et al. [6]. Further encouraging steps forward in the interpretation of the experimental and simulation results for Zr—Be amorphous systems were made by Syrykh et al. in the recent experiment on the IN4 spectrometer [11].

Investigation of modes in Zr—Be metallic glasses at low neutron momentum transfers fits well within the trends observed recently to investigate collective dynamics of fluids composed of disparate-mass atoms. For whole class of fluid mixtures, such as a rare-gas mixture [12], metallic alloy Li_{4}Pb [13], or liquid water [4, 12, 14], the emergence of two propagating 'kinetic modes' at intermediate wave vectors has been observed. In the investigations of Li_{4}Pb alloy [15] and He_{65}Ne_{35} mixture [16] a non-acoustic origin of the high-frequency mode were suggested by a neutron experiment and MD study. Bryk et al. [17] showed that such an optic-like mode could vanish abruptly in the Q → 0 limit. Computer simulation of the lattice dynamics of crystalline Li_{22}Pb_{5} was carried out by Fernandez-Perea [18]. The calculated spectrum showed several bands corresponding to modes in which only the light atoms perform motions. The results support the idea put forward by Campa [19] regarding the possibility of detecting the presence of the 'kinetic modes' even if the fluid undergoes a freezing transition.

Motivated by the ongoing spectroscopic and structural research in ZrBe binary amorphous alloys and by their timely and relevant technological applications, we have embarked on a coherent research program employing a combination of neutron diffraction (ND), inelastic neutron scattering (INS) and neutron Compton scattering (NCS). Such an approach, demonstrated previously in the neutron studies on cesium hydrogen sulfate [20] and graphite intercalation compounds [21], has proven that, when applied to the same material, ND, INS and NCS span a uniquely large time and space window that enables global modelling and optimisation of structural and dynamical models of complex systems.

NCS has proven to be very successful in characterising systems where phonon dispersion curves are difficult to characterise or resolve or at high temperatures [22, 23]. This unique feature of the NCS technique is owed to the fact that, operating in the impulsive scattering regime, NCS measures total excitation curves of all motional degrees of freedom, through nuclear momentum distributions (NMDs), in a form of a collection of Doppler-broadened recoil
peaks [22, 23]. The widths of the recoil peaks in momentum space are proportional to the first moments of atom-projected phonon density of states (apVDOS), no matter what the shape of the dispersion relation. This feature of NCS is of importance for measurements of phonon-related phenomena, like superconductivity, also exhibited by ZrBe binary systems [6], where the high-energy phonon modes are theoretically predicted but entirely confirmed experimentally. This NCS characteristic feature is in blatant contrast with structural probing techniques, like ND, where the Debye-Waller factor can be termed as the ‘minus-first moment of the apVDOS’. To this end, NCS does not suffer from typical for ND intensity decrease as the temperature of the system under investigation is increased [22, 23]. Moreover, NCS is a local probe. Namely, due to the fact the measurement of momentum distributions yields wave functions in momentum space, the NCS technique is capable of directly measuring local effective potentials felt by nuclei in mass-resolved manner and thus to characterize the degree of anharmonicity or anisotropy of those potentials. It is this very sensitivity to the individual apVDOS and the local probe character that make the NCS a very robust benchmarking technique for \textit{ab initio} predictions of NMDs, calculated both from molecular dynamics (MD) and density functional theory-based lattice dynamics (LD-DFT) [24, 25, 26, 21, 20, 22, 23, 27, 28].

Our first attempt to characterise ZrBe binary amorphous alloys concentrated on the Zr$_{40}$Be$_{60}$ system [29]. The work sought spectroscopic blueprints of phonon dispersion curves by jointly performing INS experiments at TOSCA instrument [30, 31, 32], and NCS and ND at VESUVIO instrument at Rutherford Appleton Laboratory (RAL) in the UK [33, 34]. The NCS-based characterisation of the dynamical behaviour of Zr and Be atoms has been performed, for the first time in a wide range of temperatures between 10 and 300 K. The characteristic nuclear quantum observables included the kinetic energy and standard deviations of nuclear momentum distributions. A comparison of the experimental values with the apVDOS spectra, refined by recursion method based on the data obtained with thermal neutron scattering, provided very satisfactory agreement. Also the experimental data were compared with the Debye model, which showed that the Debye temperature accounts better for the nuclear dynamics of Be nuclei than it is in the case of Zr. Interestingly, around the room temperature the nuclear dynamics of both isotopes was shown to be much less accurately accounted for by the Debye model. Moreover, the measurements at different temperatures provided an opportunity to evaluate the significance of anharmonicity in the dynamics of metallic glasses.

Continuing our line of research on the ZrBe binary amorphous alloys, this contribution reports on further efforts in multi-technique characterisation of this interesting and intriguing systems. In what follows, we will present results of joint application of ND, INS and NCS to contrast the amorphous and polycrystalline Zr —Be systems. Beside being motivated by our ongoing research programmes, both at the Kurchatov Institute and RAL, this work draws its inspiration from the seminal NCS work by Bermejo \textit{et al.} [35] contrasting hydrogen and deuterium nuclear quantum effects in crystalline and glassy environments.

\section*{2. Results and discussion}

\subsection*{2.1. Diffraction of amorphous and polycrystalline Zr —Be}

In order to monitor the structure of the samples, two independent diffraction measurements were performed. The first, before the neutron experiment, was the X-Ray characterisation, performed at the diffractometer IPDS-II at the facilities of the Accelerator Center for Neutron Research at the Institute for Nuclear Research, Russian Academy of Sciences. The X-Ray diffractogramms of amorphous and polycrystalline Zr —Be samples are shown in Figure 1.

Following the X-Ray characterisation, concurrently with the NCS data, the ND data were recorded on the VESUVIO spectrometer [29]. The ND data recorded at T=10K together with the Al sample container diffraction data at T=10K are shown in Figure 2. Both techniques, XRD and ND, yield the same result: the amorphous sample (red traces) is characterised by
Figure 1. The X-Ray diffraction data of amorphous (red trace) and polycrystalline (black trace) Zr—Be samples measured on the diffractometer IPDS-II. See text for details.

diffuse, unresolved intensity in diffraction (the only Bragg peaks visible in the diffraction data come from the Al sample container), whereas the polycrystalline sample exhibits very well resolved diffraction peaks. The amorphous data exhibit large broad peak at the d-spacing of ca. 2.5 Å in very good accordance with the partial pair distribution functions, $G_{ab}(r)$, obtained by Bratkovsky et al. [6] using the structure model of amorphous Zr—Be alloys and more recent total scattering data obtained by Golovkova et al. [36]

Further refinement of ND VESUVIO data was performed in order to elucidate the structural composition of the polycrystalline Zr—Be system. To this end, structure refinement was performed using the TOPAS V 5.0 software [37] on the polycrystalline Zr—Be sample measured at T=10K. The result of this procedure is shown in Figure 3. Data were normalised, and the contribution to ND from the Al container subtracted prior to the analysis. Rietveld refinement, within agreement factors $R_{exp} = 0.11\%$, $R_{wp} = 2.01\%$, $R_p = 4.46\%$, yielded three phases:

- The first hexagonal phase, Be$_2$Zr (ICSD code 58756), amounting to 87.11\%, was refined, within the space group $P6/mmm$, with the following lattice parameters, $a = b = 3.800(3)$ [Å], $c = 3.226(2)$ [Å].
- The second hexagonal phase, Be$_5$Zr (ICSD code 58757), amounting to 12.89\%, was refined, within the space group $P6/mmm$, with the following lattice parameters, $a = b = 4.564(3)$ [Å], $c = 3.477(2)$ [Å].
- The third phase of unspecified stoichiometry but contributing to the overall improvement of the refinement, of orthorhombic space group, with the following lattice parameters, $a = 9.737(8)$ [Å], $b = 4.577(3)$ [Å], and $c = 3.072(3)$ [Å].

The results of the refinement are shown in Figures 4 and 5. Taking into account, the stoichiometric composition of both phases and their percentage contributions to the entire ND signal, obtained from refinement, the effective sample formulation yields Be$_{70}$Zr$_{30}$. Work is in progress, to calculate, based on the refined structure composition, the apVDOS and hence NMDs of Zr and Be within the LD-DFT method. This approach may prove superior to the recursion method, as the former is, in principle able to discern different contributions to the VDOS stemming from different structures present in the system under investigation, despite the same net sample stoichiometry. Moreover, LD-DFT is in principle capable of contrasting the
Figure 2. Neutron diffraction data of amorphous (red trace) and polycrystalline (black trace) Zr—Be samples recorded concurrently with NCS data at the VESUVIO spectrometer. Additionally, Al container diffraction pattern is shown as green trace. See text for details.

prediction for polycrystalline and amorphous phase, despite their identical formulation. The task envisaged here proves, however, very difficult due to the presence of the third phase and possible additional trace admixture of the amorphous phase.

2.2. INS and NCS
Inelastic and deep inelastic neutron scattering spectra were recorded on Tosca and VESUVIO spectrometers, respectively, both located at RAL [30, 31, 32, 33]. The details of the instrumental setup and the data reduction and analysis procedures have been extensively described elsewhere for both instruments. Thus, in what follows, we will provide a slightly alternative description aiming to emphasize the synergies, both at the instrumental and data analysis level, created by the strategy to collect and analyse INS and NCS data concurrently on the same system.

Also from the sample preparation point of view, both instruments present a favourable case as they can use the same sample container design, which can greatly facilitate the streamlining of multi-instrument global studies like the one presented here, especially in case of parametric studies as a function of external stimuli, like temperature. In the particular case of the experiments described here, both Zr—Be samples were measured as enclosed in a 6x6 cm² flat aluminum (Al) cells. The resulting total sample transmission was 92% for the polycrystalline and 87% in case of the amorphous sample, with the scattering power of the Al container identical and equal to 2% in both cases. The data used in the analysis described here were recorded at T = 10, 200 and 300K with the sample and container temperature stabilised using a dedicated helium closed-cycle refrigerator. With the average proton charge to the TS1 target of 165 μAhrs in case of both samples, the average time of both the NCS and INS experiments was 12 hours per sample per temperature.
Figure 3. Neutron diffraction data of polycrystalline Zr — Be sample recorded at T=10K concurrently with NCS data at the VESUVIO spectrometer. Blue line - Be$_2$Zr phase, black line - Be$_5$Zr phase, green line unknown Be-Zr phase, red line - experimental ND data, violet line – residual. See text for details.

Figure 4. The unit cell of the first phase (ICSD code 58756), amounting to 87.11%, identified by Rietveld refinement of ND VESUVIO data. Eight Zr atoms contributing 1/8 and two Zr atoms make up the Be$_2$Zr unit formula. See text for details.
Tosca and VESUVIO are located at the Target Station 1 of the ISIS pulsed neutron and muon source at RAL. Both are inverted geometry instruments using a polychromatic broadband incident neutron beam viewed from sample position via water moderator. Moreover, both instruments use the same strategy to harness the full power of the ISIS source. Namely, as ISIS arranges the incident neutrons in pulses with the period between them being 20 ms (a sub-frame), both instruments are set up to receive 4 pulses in a single frame while the last pulse of the source is redirected towards the second target station [30]. Both Tosca and VESUVIO exploit the missing pulse to extend the energy transfer range of the instruments by measuring neutrons in the high time-of-flight (TOF) region. Tosca, measures the high TOF region neutrons to access the intense elastic line. On VESUVIO this high TOF region was previously extended to access the neutron energy range down to 1 meV quite successfully, extending the dynamics range of high resolution VESUVIO backscattering banks to access lattice spacing values in the range of ca. 7 Angstrom [38].

The INS spectra of amorphous and polycrystalline Zr—Be samples recorded at Tosca at T = 10K are shown in Figure 6. The recorded spectra agree very well with the atom-projected VDOS curves calculated by Bratkovsky et al. [6] by means of the recursion method, shown in the inset in Figure 6 as adopted from Ref. [6]), when one takes into account the sample stoichiometry and neutron neutron cross section weighting.

Figure 6 is the best starting point to briefly describe the NCS data analysis drawing from the analogies between the INS and NCS. Namely, in an INS spectrum both components of the atom-projected VDOS merge as a total, neutron-weighted (multiplied by the respective neutron

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**Figure 5.** The second phase (ICSD code 58757), amounting to 12.89%, identified by Rietveld refinement of ND VESUVIO data. Eight Zr atoms contributing 1/8 and five Zr atoms make up the Be$_5$Zr unit formula. See text for details.
Figure 6. The INS spectra of amorphous (blue trace) and polycrystalline (black trace) Zr—Be samples recorded at Tosca at T = 10K. Inset: Partial densities of states, ga_{Zr}(E) and ga_{Be}(E), of Zr and Be respectively, calculated for a series of three amorphous systems Zr_{1-c}Be_{c} with c = 0.3, 0.4 and 0.5. Figure adopted from Ref. [6]. The curves are calculated using the structure model for c = 0.3 (full line), 0.4 (dashed line), and 0.5 (dotted lines). See text for details.

scattering cross-sections of Zr and Be) spectrum. This INS feature disables a detailed dissection of spectra into atom-projected contributions. Such a dissection could be in theory only performed from INS data in the lucky case of completely non-overlapping sets of INS modes stemming from two different nuclei. As one can see in Figure 6, even in case of such mass disparity as the one exhibited by Zr and Be in Zr—Be systems this task cannot be fully achieved. This clearly demonstrates the need for a method that does not suffer from ‘coupling constant weighting’, a method such as NCS. NCS, operating in the kinematic regime of up to hundreds of electron-Volt incident (termed as epithermal) neutron energies, and up to tens of Å^{-1} of momentum transfer from neutrons to nuclei in the target sample, fulfils the assumptions of the Impulse Approximation (IA) [39, 24, 23]. In consequence, a billiard-ball type of scattering between the neutron and each nucleus in a sample leads to the creation of a TOF spectrum, consisting of a series of separate recoil peaks, each coming from the longitudinal momentum distribution of each nucleus in the sample. Moreover, the intensity of each NCS recoil peak scales with the product of its total bound scattering cross-section and the total number of atoms of given type in the incident neutron beam [39, 24, 23], thus rendering the NCS method completely free from the ‘neutron weighting problem’.

The second, very important in the context of the presented joint INS and NCS data and the global modelling approach to Zr—Be systems under investigation, NCS feature is that the individual recoil peak shapes, when transformed from TOF to longitudinal momentum transfer domains to form nuclear momentum distributions, NMDs, are, to a good approximation
the Born-Oppenheimer approximation [40, 26] as:

$$\sigma_{Mn}(\hat{q})^2 = \frac{M_n}{N_q \hbar^2} \sum_{q \in BZ} \sum_{\lambda=1}^{N_\lambda} (e_n(\lambda, q) \cdot \hat{q})^2 \frac{\omega(\lambda, q)}{2} \coth \left( \frac{\omega(\lambda, q)}{2k_BT} \right),$$  \hspace{1cm} (1)

where \( \omega(\lambda, q) \) are phonon frequencies, \( e_n(\lambda, q) \) are polarization vectors and \( T \) is the sample temperature. The double summation in Eq. 1 runs over all \( N_q \) vectors in the first Brillouin zone, and all phonon branches \( N_\lambda \).

From Eq. 1, the spherically averaged value of the second moment of the nuclear momentum distribution for a given nucleus \( n \), \( \sigma_{Mn}(\hat{q})^2 \), can be calculated as [41]

$$\sigma_n^2 = \frac{1}{3} \left[ \sigma_n(\hat{z})^2 + \sigma_n(\hat{y})^2 + \sigma_n(\hat{z})^2 \right]$$  \hspace{1cm} (2)

Interestingly, in the context of the atom-projected VDOS data shown above, yet another method of the NMD widths calculation has risen to popularity, the recursion method [9]. In a nutshell, recursion method amounts to recursively by tri-diagonalizing the dynamical matrix describing the forces in a basis of orthonormal operators [9]. This method can lead to substantial acceleration of computational effort, as compared to LD-DFT. By exploiting the system symmetry, or lack of long-range order, the dynamical matrix can be greatly simplified and described by a handful of force constants.

In what follows, we will complement already published data on the amorphous Zr\textsubscript{40}Be\textsubscript{60} system [29] with new data collected on the Zr\textsubscript{40}Be\textsubscript{60} system which is polycrystalline. The NCS data treatment protocols are described elsewhere in great detail [24, 23, 25, 26, 42]. Here, we will only briefly mention those aspects of the particular data reduction that were crucial for extraction of the NMD widths and nuclear kinetic energies in case of the specific systems under investigation. Specifically, for the NCS data analysis on both Zr—Be systems data recorded in backscattering were exclusively chosen due to much better mass-separation, much needed in case of three disparate nuclear masses, of 9 (Be), 27 (Al), and 91 (Zr) atomic mass units. The NCS backscattering data analysis can be summarised in the following steps:

- Raw backscattering TOF data were fitted sequentially detector by detector using Equation:

\[
C_q(t) = A'\frac{E_0I(E_0)}{Q} \times \sum_{n=1}^{N} I_n M_n J_n[y_n(t)] \otimes R_n[y_n(t)]
\]

(3)

where \( A' \) is a mass–independent experimental constant and the mass–independent factor \( \frac{E_0I(E_0)}{Q} \) depends on the incident neutron spectrum, \( I(E_0(t)) \), the initial neutron energy, \( E_0(t) \), and the momentum transfer \( Q(t) \), all explicit functions of \( t \), \( J_M(y_M(t)) \), are NMDs of nuclei in the sample in the IA limit with integrated peak intensities \( I_M \) proportional to the scattering densities and total (bound) neutron-scattering cross sections, \( I_M = AN_M4\pi b_M^2 \) where \( 4\pi b_M^2 \) is a total (coherent plus incoherent) bound neutron scattering cross section.

- the obtained values of the fitting coefficients, \( I_M \) and \( \sigma_M \) were used as input parameters to calculate the sample-dependent back scattering corrections due to multiple scattering (MS) from the sample and container;

- after subtraction of the MS contributions, a cumulative sum of weighted TOF spectra was formed with spectra normalised by the total TOF integral and summed in three groups of
backscattering detectors: 3-46, 47-90, and 91-134. Each sum of normalised detector data was fitted with a respective sum of TOF-normalised fitting curves, each member of the sum described by Eq. 3, i.e., \( \sum_{i=1}^{N} C(\theta_i, t) \). Underlying NMDs for all nuclei were assumed to be the sums of a pure Gaussian with standard deviations, \( \sigma \) and an additional term, proportional to a Gaussian multiplied by a third-order Hermite polynomial, accounting for the departures from the IA approximation, termed as Final States Effects (FSEs), with FSE magnitude \( k \) constrained within the harmonic approximation to \( k = \sqrt{3/12} \sigma \). This method, referred to as CAAD, has been already successfully tested in treatment NCS data in Mass-selective Neutron Spectroscopy (MANSE) beyond the proton [24, 23, 43].

- The fitting parameters for each cumulative sum were the 3 values of NMD widths and 3 values of NMD relative intensities of Be, Al, and Zr. No stoichiometric fixing was employed in order to check the obtained sample stoichiometry against the diffraction data, collected concurrently on VESUVIO. In what follows, we will present the results of the CAAD analysis for the first group of detectors as the NCS data collected from detector 3-46 were found to exhibit the best signal-to-noise and background ratios and best mass-separation due to relatively high scattering angle values.

The first result coming from the CAAD fitting, is shown in Figure 7. The first observation is that, due to different total scattering power, greater in case of the amorphous sample, the share in the total CAAD curve, of the Al container recoil peak is smaller. However, in case of both samples the scattering power levels are good, thus resulting in overall good signal-to-noise ratios and enabling precision NMD fitting. This result demonstrates why the CAAD method was chosen for data analysis in this particular case. Namely, the method has the advantage of retaining the mass-resolution contrast in the data for better visualisation but capitalises on the cumulative nature of the signals of nearby detectors to maximise the signal to noise ratio and reduce otherwise high degree of data sparsity. The CAAD method proves robust for the determination of both NMD widths and relative peak intensities of both Be and Zr. To demonstrate this, we first mention that the relative intensities of the polycrystalline sample were, as averaged over all three temperatures of measurement and detectors 3-46, 0.23 ± 0.01 for Zr and 0.54 ± 0.01 for Be. This, gives the effective sample stoichiometry of \( \text{Be}_{70}\text{Zr}_{30} \), to within 2% accuracy identical to the one obtained from the ND studies, reported above. The values for the amorphous \( \text{Zr} — \text{Be} \) system are 0.34 ± 0.01 for Zr and 0.56 ± 0.01 for Be, yielding the stoichiometry \( \text{Be}_{60}\text{Zr}_{40} \) to within 2% accuracy equal to the values reported in our previous work [29].

The results can be better summarised in form of a table (Table 1) comparing the values of the the kinetic energies of Be and Zr, in both Zr — Be systems. The values reported are contrasted with theoretical predictions, from the Debye and recursion methods. Importantly in this context, the predictions of the VDOS and nuclear kinetic energy from the recursion method depend only on the short range order. It is thus expected that, as far as the local order dictating the high-frequency modes is concerned, the recursion method provides reliable predictions for both polycrystalline and amorphous systems. The most striking feature, present consistently at all temperatures is that the polycrystalline sample exhibits significantly (above the value of one standard deviation) higher value of the kinetic energy for both Zr and Be nuclei. This result is in line with the result of pioneering work by Bermejo et al. [35], where differences of ca. 6 meV in kinetic energy were observed for hydrogen (H) and deuterium (D) between polycrystalline and amorphous glasses in the temperature range from 10 to 110K. Following the authors of this seminal work [35], we will mention here that the low temperature regime of both studies, (i.e., between 10 and 200K), minimises the chances of anharmonic effects to manifest themselves and the response of the 'lattice' is dominated by one-phonon terms. In this spirit, the low temperature results show already another two important trends. Firstly, the experimental results for the
polycrystalline sample show more convergence towards the theoretical values obtained from the recursion model, thus taking into account albeit short range but still local order. The differences between the polycrystalline and amorphous samples in terms of their kinetic energies are smaller than it was the case for H and D in glass samples investigated by Bermejo et al [35] due to the fact that both Be and Zr are, in the sense of their Zero Point Energy values (ZPEs) much more classical in nature than it is the case for H and D. This means that their momentum distributions, even in the chemically bound state, resemble more those of systems of classical non-interacting gas particle, the celebrated Maxwell-Boltzman distribution [22, 23]. In this spirit, a yardstick of the degree of nuclear momentum distribution modification due to chemical binding and ordering was proposed in NCS work on cesium hydrogen sulfide. [20] The variable introduced there, the quantum energy excess, QE, was defined as ratio of experimental to classical kinetic energy.
\[ E_{\text{cl}} = \frac{3}{2} kT, \]
where \( k \) is the Boltzman constant and \( T \) the temperature [20]. The values of \( E_{\text{cl}} \) are mass independent and yield 1.29, 25.8 and 38.8 meV at \( T=10K \), 200K, and 300K, respectively. The QE values range from as much as 23.26 for polycrystalline Be at 10 K to 1.16 for amorphous Zr at 300K (see Table 2). The general trend is that the QE values for the polycrystalline system are systematically higher than those for the amorphous one, both for Be and Zr (see Table 2). In the spirit of the QE, we can say that both Zr and Be exhibit a larger degree of binding and ordering in the polycrystalline system, independently on the temperature and degree of system anharmonicity.

Table 1. The value of kinetic energies of Zr and Be in amorphous and polycrystalline Zr—Be system (in brackets). All values of the kinetic energy are in meV and the values of temperature in K. See text for details.

| \( T [K] \) | Theory \( E_{Zr} \) | Experiment \( E_{Zr} \) | Debye Theory \( E_{Zr} \) | Experiment \( E_{Be} \) | Debye Theory \( E_{Be} \) |
|------------|----------------|----------------|----------------|----------------|----------------|
| 10         | 18             | 15 ± 1 (16 ± 1) | 14.0           | 26 ± 1 (30 ± 1) | 28.4           |
| 200        | 36             | 32 ± 1.5 (38.9 ± 1.3) | 28.4 | 47 ± 1.5 (51.9 ± 1.3) | 50.1 |
| 300        | 46             | 45 ± 2 (47.1 ± 1.5) | 40.0           | 62 ± 2 (64.6 ± 1.3) | 58.8 |

Table 2. The values of quantum energy excess, QE, of Zr and Be in amorphous and polycrystalline Zr—Be system (in brackets). See text for details.

| \( T [K] \) | \( QE_{Zr} \) | \( QE_{Be} \) |
|------------|--------------|--------------|
| 10         | 11.63 ± 0.78 (12.40 ± 0.77) | 20.16 ± 0.78 (23.26 ± 0.78) |
| 200        | 1.24 ± 0.06 (1.51 ± 0.05) | 1.82 ± 0.06 (2.01 ± 0.05) |
| 300        | 1.16 ± 0.05 (1.21 ± 0.04) | 1.60 ± 0.05 (1.66 ± 0.03) |

The fact that the kinetic energies of the polycrystalline Zr—Be system are systematically higher than the values for its amorphous counterpart has one more very important consequence. Namely, as mentioned in the beginning of this section, the second moments of the NMDs can be termed as first moments of the atom-projected VDOS. Thus, the presence of a previously unaccounted for mode, like an optical mode, associated with high frequency vibrations, will be signalled in NCS by the increase of the NMD width as the first moment of the VDOS will shift to the higher frequencies. Glasses and polycrystalline samples present an interesting case in this respect. As reported more than two decades ago by Bermejo et al [35], glasses had been already then subject to heated debate in the literature as to the origin of the low-frequency modes, known to be responsible for most of the thermal and transport anomalies in disordered matter. Highly localised soft modes had been at that time made mainly responsible for this phenomenon, with the soft modes postulated to be either already existing in the crystalline state, or alternatively, to be already present in the glasses. Drawing the motivation from the very same study of Bermejo [35], we can seek the origins of different dynamical response of amorphous and polycrystalline Zr—Be systems to dynamics anomalies in glass formation, visible in the energy-momentum window of the NCS method. In doing so, we will account for the difference between
the glassy and crystalline environments by approximating the overall NMD profiles of Zr and Be as a convolution of the local and lattice modes, assuming the local modes to give numerically the same contribution to the kinetic energies of both nuclei. Work is in progress to account for the lattice modes of the crystalline phase found in the ND refinement described above. As this will require some computational effort as far as LD-DFT or MD is concerned, here we will thus only give a quick assessment using the experimental results. In the following, we will only use the 10K values to avoid possible complications arising from the anharmonicities in the both systems. As can be seen from Table 1, the differences in kinetic energies for Zr are ca. 1 meV at 10K. The corresponding values for Be are ca 4 meV at 10K. These values lie outside the energy regime investigated recently by INS spectroscopy using IN-4 and BRISP spectrometers, where opposite direction trends of phonon dispersion lines were discovered for low (ca 14 meV) and high (ca 45 meV) energy modes. The high-energy modes were thus shown to be largely independent from type of disordered system composed of Zr and Be [44]. The low frequency modes, however, may be exhibiting softening behaviour and their dispersion curve may differ from system to system, depending on the nature of the local order or disorder of the glassy matrix. Thus, on the whole, it seems to be more plausible that the low-frequency mode band centered at ca 15 meV softens when going from crystalline to glassy environment in the Zr—Be systems under investigation.

2.3. Summary and outlook
In conclusion, exploiting the the unique tandem of VESUVIO and Tosca inverted geometry spectrometers, in case of VESUVIO augmented with the capability to perform high resolution diffraction, has led to a number of interesting results shedding more light on the possible origins of disorder in Zr—Be binary mixtures by comparing ND, INS and NCS data recorded for the polycrystalline Zr$_{30}$Be$_{70}$ and an amorphous Zr$_{40}$Be$_{60}$ systems.

Firstly, the phase assignment of the polycrystalline Zr—Be system led to the prediction of sample stoichiometry, thus corroborating the NCS results. The unique combination of INS, NCS and ND has lead to the elucidation of the structural and dynamical features responsible. Secondly, the INS data were cross-validated by the NMDs of both Zr and Be, obtained from NCS. Finally and most importantly, the crystalline Zr—Be system showed systematically higher values of kinetic energies of Zr and Be, as compared to its amorphous counterpart. A plausible explanation of this trend, present at all temperatures from ambient down to 10 K, is due to low-frequency vibrational mode softening, when going from crystalline to the amorphous phase.

On the theoretical front, the INS and NCS analysis provided a robust benchmarking for the theoretical results obtained from the recursion method. To this end, the small deficiency of the recursion method to account for the long range order in the crystalline system was exposed by the NCS, emphasizing the need for \textit{ab initio} calculation. To this end, the results of the diffraction analysis have provided structural information for the ongoing further structure elucidation and \textit{ab initio} nuclear dynamics work by employing DFT-based lattice dynamics and molecular dynamics.

On the whole, the work has provided clues as to hitherto unexplored aspects of origins of structural and dynamical differences between the order and glassy environments, thus paving the way for future global studies with more challenging, structurally complicated materials of technological relevance.

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