Response of crystalline and amorphous metallic alloys to pulsed THz radiation

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For almost five decades metallic glasses have been subject of great interest due to their particular and novel properties that are unusual for solid metals. Although commercial applications of metallic glasses are increasing, there is still a limited knowledge on some of their properties. In this project we study the response of metallic glasses in the THz frequency range, where a strong anomaly in the vibrational spectrum, known as *Boson Peak*, has been reported. In order to study the existence of this anomaly both pure metals and metallic glasses have been analyzed by means of a time-domain spectroscopy technique. Afterwards, both metallic glasses and pure metal's results will be compared in order to study if the Boson Peak is intrinsically characteristic of metallic glasses.

I. INTRODUCTION

Metallic glasses are structurally disordered alloys without long-range periodic atomic order. They are usually manufactured by rapid quenching, by cooling the molten alloys at high cooling rates, up to 10^6 K/s. The lack of the crystalline structure gives rise to some remarkable mechanical properties, such as high strength and large elastic limit as compared to its crystalline counterparts. However, the lack of knowledge or explanation on some of their properties still restricts their use in certain applications. Their mechanical response, for instance, is closely related to their vibrational spectrum. Whereas crystalline-lattice dynamics is well understood in terms of phonon dispersion, the vibrational spectra of glasses has some specific features which differ considerably from those of crystals, and its theoretical interpretation is a matter of controversy.

It has been found that metallic glasses present strong deviations from the predictions in the Debye's model in the low frequency range. Roughly one order of magnitude below the Debye's frequency, the vibrational density of states $g(\omega)$ of almost all glasses deviates from the Debye's quadratic law, showing up as a maximum in the reduced density of states, $g(w)/w^2$. This maximum has been called "Boson Peak" (BP), and appears in the THz energy range. The Boson peak is related to another anomaly of the specific heat of glasses at temperatures of $\sim 10K$. In this regime Debye's theory establishes a $C_V \; \alpha \; T^3$ dependence, but the function $C(T)/T^3$ shows a maximum which has also been called the Boson Peak [1][2].

The vibrational spectrum of glasses can be obtained by Inelastic Scattering techniques, either of neutrons (INS) or X-Ray (IXS). In the case of metallic glasses, IXS measurements showed two specific features. On the one hand, the frequency dependence of the sound attenuation, a measure of the energy loss of sound propagation in media, shows a strong increase near the BP frequency. And, on the other hand, some experiments report an increase of the phase sound speed at frequencies in the THz range[3]. The sound speed is related to the bulk modulus that measures a material resistance to uniform compression [4]. Changes in the bulk modulus have a direct impact on the mechanical properties of the glass. The physical origin of these properties has been lively discussed for many decades; however, an agreed on solution is still lacking. The increase on the bulk modulus in the THz range may imply the appearance of a resonance in this frequency range. Here we use a time-domain spectroscopy technique to study the response of metallic glasses in the THz frequency range and its possible connection to the increase of the bulk modulus and the properties of the Boson peak.

II. EXPERIMENTAL

The experimental setup is depicted in Figure 1. Measurements were performed by using a commercial Time Domain Spectrometer (Menlo TERA-K8). It consists of a pulsed femtosecond laser at 780 nm with a pulse repetition rate of 100 MHz and a pulse width around 110 fs,

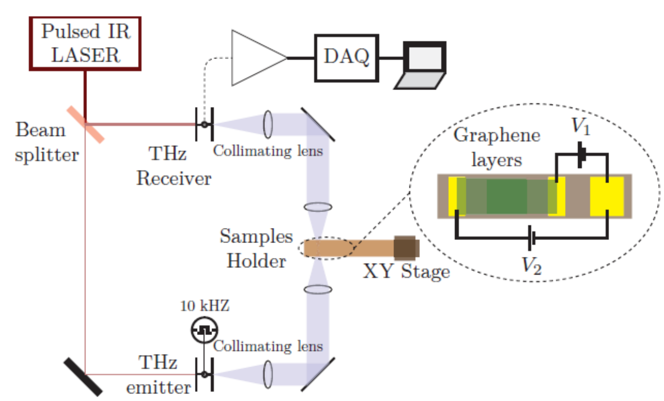

FIG. 1. Schematic view of the THz time-domain experimental setup employed to characterize the samples illustrating the disposition of the samples and voltage sources.

offering with the current experimental setup a signal-to-noise ratio of 40 dB up to 2.5 THz. Two photoconductive antennas based on LT GaAs (Tera8-1) are used to generate and detect the THz radiation. Then, a set of lenses focuses the THz beam onto the sample under measurement. The total sample area illuminated by the beam is roughly $2mm^2$. A more detailed description of the experimental system can be found in [5].

The experiment was designed to determine if the response of metallic glasses to THz radiation is different than that of crystalline metals. A representative set of Metallic glass samples of different compositions were provided by Profs. P. Bruna and D. Crespo. These samples had been produced by rapid quenching. Precursor alloys of 5-10 g were produced by arc melting, and subsequent ribbons were produced by melt spinning in a cold wheel. The ribbons were about 1 mm wide and $30\mu m$ thick. The samples were produced prior to the experiments, and some of them were produced several years ago and stored at room temperature. To allow comparison to crystalline metals, similar ribbons of pure Cu, Al and Ni were produced by the same procedure for this experiment.

Measurements were performed by moving the sample normal to the beam and taking a measurement every 1 mm. Assuming that the beam is transmitted through the sample, the transmitted signal is the convolution of the incident beam and the transmission factor. Thus, the transmission factor in the frequency domain can be obtained by dividing the Fourier transform of the signals obtained with and without sample. The analysis was restricted to the frequency region between 0.3 and 3 THz, due to two facts. On the one hand, the frequency power spectrum of the incident pulse above 3 THz decays exponentially, thus the effect of noise increases with frequency. And, on the other hand, the differential absorption is expected about 1 THz.

Several sets of data corresponding to each of the positions across each sample were obtained. Given the sizes of the beam and the sample, the successive elements of each set begin with the measurement out of the sample, that is in air, followed by measurements of sample plus air, sample, sample plus air and finally air again.

III. RESULTS AND DISCUSSION

Figure 3 shows the results obtained in a $Pd_{40}Ni_{40}P_{20}$ metallic glass sample. Left to right, the first figure shows the transmission factor of the beam passing partially through air and partly though the sample. The second figure corresponds to the beam passing through the sample. The third figure corresponds again to a beam passing partly though air and the sample, and the last figure corresponds to the beam passing outside the sample. The differential absorption of the sample is very high, as it is expected in a metallic glass material which should absorb completely the electromagnetic beam. The first and third figure show a similar trend. Both exhibit an absorption peak at frequencies around 0.4 THz. The fourth figure shows the differential spectrum of air, and allows us to set limits to the precision of the measurement. The high oscillations observed above 2 THz show the increase of the noise in the measurement.

As for the crystalline ribbons, Figure 2 shows the response of the pure Al sample. Contrary to $Pd_{40}Ni_{40}P_{20}$ the sample does not show an absorption peak at low frequencies. However, the Ni metallic ribbon - not shown - presented also an absorption around 0.4 THz like metallic glasses. Then, we prepared a sample with different widths of Cu ribbon in order to see clearly if the diffraction pattern played such an important role and the results made clear that it was the main reason of the non zero transmittance intensity received, see Figure 5.

The response of different metallic glasses varied according to their age. Some of the metallic glasses older than ten years didn't show the differential absorption around 0.4 THz as shown in Figure 4. This effect may be due to long term relaxation at room temperature.

It has to be noted that measurements performed on different days presented slight discrepancies. The measuring system is very sensitive to environmental conditions such as moisture. Therefore, in order to obtain more reliable measures, the analysis should be performed in an environment lacking of moisture. Thus, we considered to perform the measurements in Nitrogen atmosphere to minimize the environmental perturbations, but the tight timetable for the project did not allow us to implement this improvement.

The analysis of the experimental data must take into account the geometrical constraints. The penetration depth in metals is

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}}$$

which in the case of Cu gives a value of $1.17 \cdot 10^{-10} m$. While the specific values vary, the order of magnitude is the same for all the considered metals. The conductivity of metallic glasses is lower than that of crystalline metals but not much lower. Our ribbons had a with of around $30\mu m$ so we should obtain zero transmission when the beam is at the center of our sample. The fact that we obtain around a 50% transmission in most cases shows that the beam width is greater than the nominal specification.

These considerations indicate that, almost in all cases, the beam hits only partially the sample. The recorded signal must contain the unaffected beam - passing outside the sample - plus diffraction and/or absorption effects on the sample edge. As the wavelength of the incident radiation is much smaller than the sample size, diffraction effects should not alter the beam spectrum; thus, changes in the beam spectrum may be attributed to absorption effects in the sample edge.

The fact that the recorded signals contain always part of the original beam makes us consider that the signal

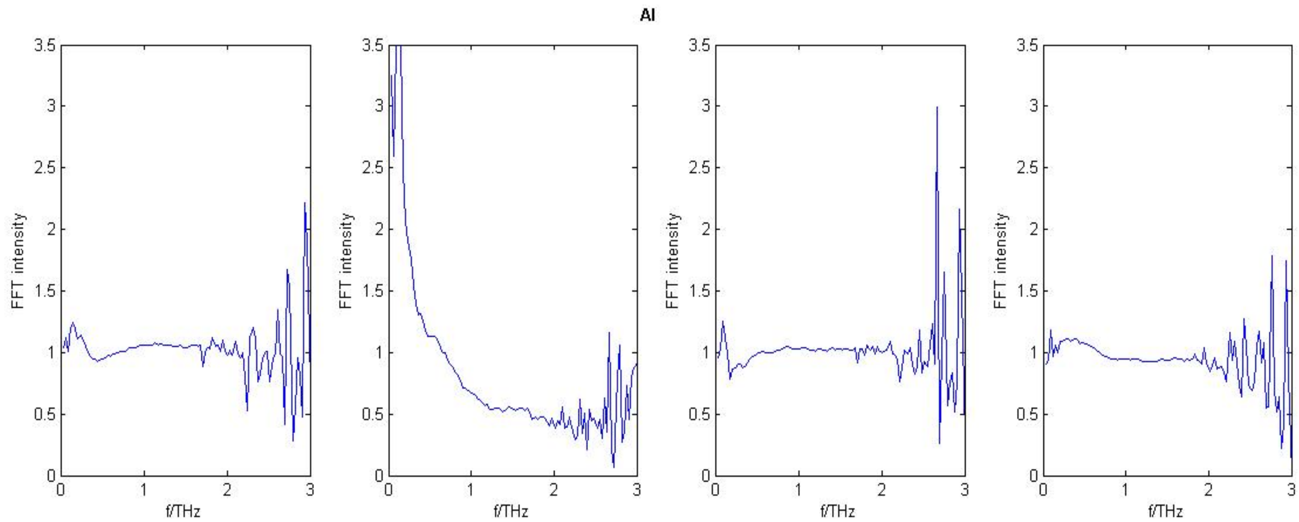

FIG. 2. Transmission factor for pure Al. **Left**: Beam outside the sample. Noise becomes important above 2 THz. **Left center**: Beam hitting the sample, showing almost null transmission. **Right center**: Beam hitting partially the sample, showing no absorption peaks. **Right**: Beam outside the sample.

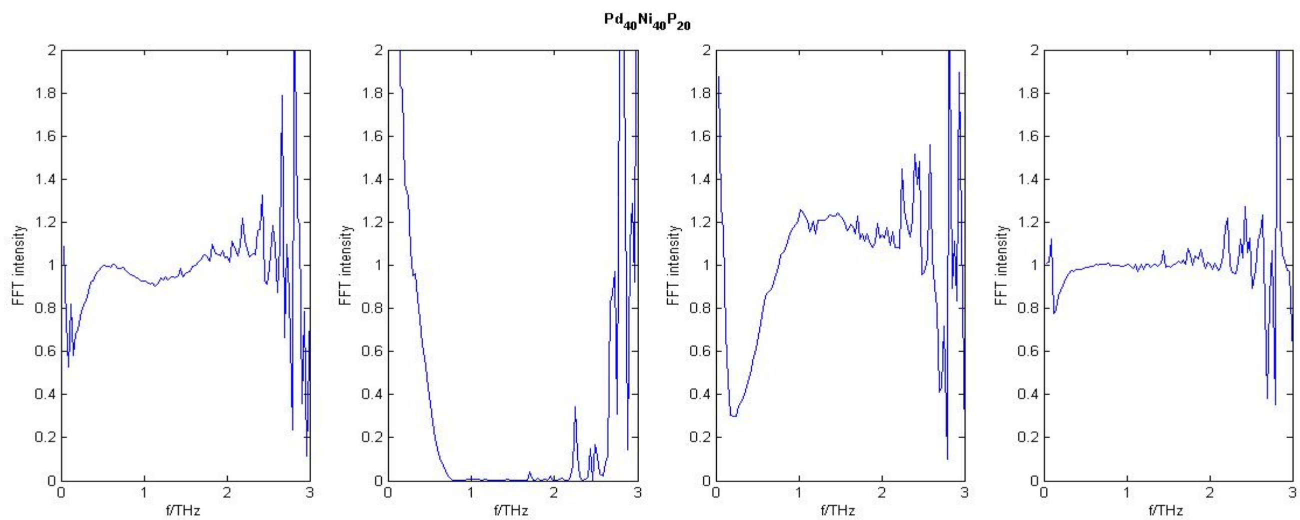

FIG. 3. Transmission factor for $Pd_{40}Ni_{40}P_{20}$. **Left**: Beam hitting the sample in one edge. Note an absorption peak around 0.35 THz. **Left center**: Beam hitting the sample, showing almost full absorption. **Right center**: Beam hitting the sample in the opposite edge, showing a much more prominent absorption peak around 0.35 THz. **Right**: Beam outside the sample.

processing is too simplistic and a treatment allowing to remove the free-beam component may be necessary.

IV. CONCLUSIONS

The response of amorphous and crystalline metallic ribbons to THz radiation was measured. Geometric restrictions showed to be determinant on the recorded data. The size of the beam is comparable to the sample width. This indicates that diffraction effects are present in the recorded signal. Furthermore, it indicates that the standard treatment of the signal as a transmitted signal is too simplistic, and a processing that allows to remove the signal component passing outside the sample may be needed. Metallic glasses showed a distinct absorption peak around 0.3 - 0.4 THz. This peak seems to vanish in old samples (produced 10 years ago or more). This effect may be related to room temperature relaxation of metallic glasses. Crystalline materials showed scattered results. While Al didn't show absorption, Ni showed absorption in the same frequency range than metallic glasses.Given that the wavelength of the incident radiation is much smaller than the sample size, the frequency response is attributed to absorption in the sample edge.The measurement technique showed to be very

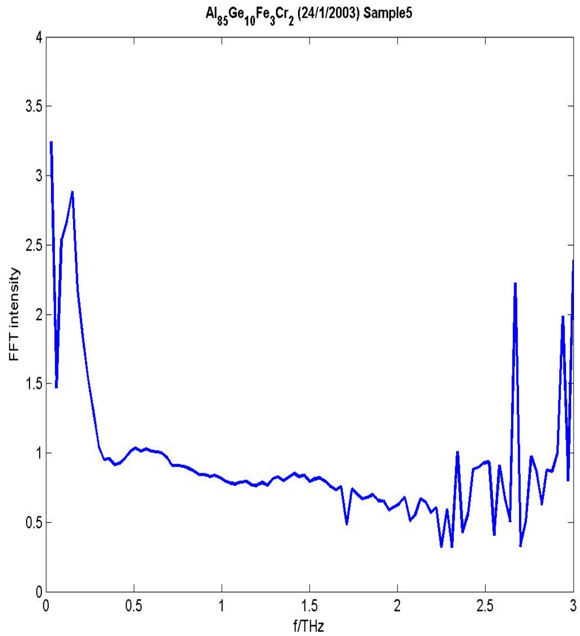

FIG. 4. Transmission factor for $Al_{85}Ge_{10}Fe_3Cr_2$ metallic glass sample, dated on 21/1/2003. The sample does not show an absorption peak at low frequencies.

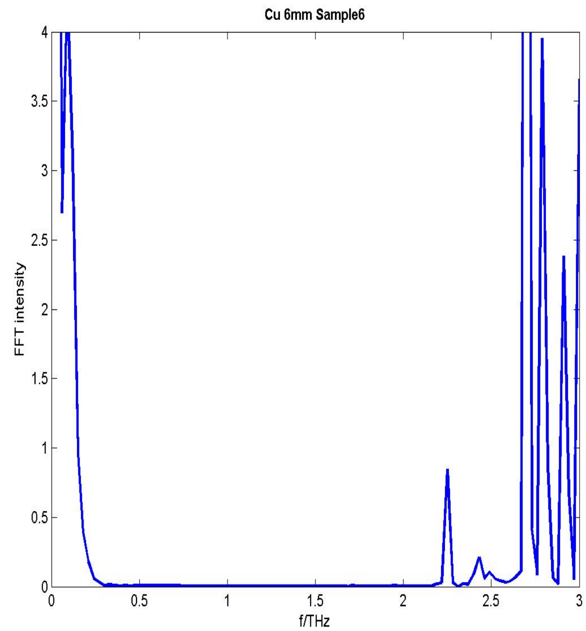

FIG. 5. Transmission factor for pure Cu 6mm wide.Unlike other ribbons ,which wide was about 1mm, the transmittance is almost zero. This shows the important role the diffraction pattern plays in our measurements.

sensible to ambient conditions, in particular air moisture content. Measurements in dry Nitrogen may result in a much noiseless response. Summarizing, although the results are not conclusive, metallic glasses seem to show an specific absorption peak which is related to its relaxation state and might be related to the Boson Peak. More work is needed, improving the experimental conditions, to clarify the response of amorphous and crystalline metallic alloys in the THz range.

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