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We report an innovative high pressure method combining the diamond anvil cell device with the technique of picosecond ultrasonics. Such an approach allows to accurately measure sound velocity and attenuation of solids and liquids under pressure of tens of GPa, overcoming all the drawbacks of traditional techniques. The power of this new experimental technique is demonstrated in studies of lattice dynamics, stability domain and relaxation process in a metallic sample, a perfect single-grain AlPdMn quasicrystal, and rare gas, neon and argon. Application to the study of defect-induced lattice stability in AlPdMn up to 30 GPa is proposed. The present work has potential for application in areas ranging from fundamental problems in physics of solid and liquid state, which in turn could be beneficial for various other scientific fields as Earth and planetary science or material research.

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Acoustic properties of solids and liquids are very sensitive to subtle changes in local or long-range order which thus make experimental measurements of phonons velocity and absorption under high pressure one of the most useful probe of interatomic potentials variations. In addition to provide a crucial test for modern ab initio calculations or Earth and planetary models, elasticity under extreme conditions substantially contributes to the understanding of phase transition mechanisms or structural stability. In a same manner, attenuation measurements provide useful information on relaxation processes for understanding the correlation between acoustic waves and intrinsic excitations. However, to our knowledge no acoustic attenuation as a function of pressure has been published and only few specialized institutions have the capability of measuring in laboratory sound velocity under high pressure and high or low temperature. Experimental methods could be classified into two types: (i) the conventional pulse-echo ultrasonic technique (acoustic wave generated by a piezoelectric transducer) combined with a large-volume cell able to accommodate sufficiently large samples so that successive echoes do not overlap [1, 2], and (ii) the Brillouin scattering in diamond anvil cell (DAC) [3]. The price to pay for the first method is the centimeter dimensions of the experimental volume, more than 4 orders of magnitude over the capabilities of DAC devices, and for the second one the transparency of the sample. In spite of many efforts to improve the pressure range, both constraints still preclude studying the elastic properties in laboratory of opaque materials under pressure above 10 GPa. In this Letter, we report a novel approach, the picosecond ultrasonics technique in diamond anvil cell, which can be easily set-up in laboratory and circumvents all previous limitations[4]. The main other advantages can be summarized as follows. It covers a large frequency range (from 1 GHz to 300 GHz) that bridges the frequency gap between the usual laboratory techniques (from 1 MHz to 30 GHz with ultrasonics and Brillouin scattering) and the large instruments one (from 1 to 10 THz for inelastic neutron or X-ray scattering). It opens a way of determining acoustic attenuation pressure dependence. And, last but not least, it can be applied to the study of any materials.

Time-resolved picosecond optical measurement in DAC will be first described. The capability of this method will then be demonstrated through the generation and detection of longitudinal hypersonic sound waves in a single-quasicrystalline icosahedral AlPdMn up to 30 GPa using Ne or Ar as pressure transmitting medium (PTM). Several reasons justify to select the ternary alloy $Al_{68.2}Pd_{22.8}Mn_9$ for this study. It is one of the metallic sample which can be routinely obtained with a high degree of structural perfection and be prepared as thin platelets of excellent polishing quality. As a consequence, its acoustic properties are free from grain diffraction or macroscopic defects such as surface roughness. The second reason is related to the crucial role that play the acoustic data in the on-going debate of the entropy contribution to the quasicrystals (QCs) stability[5]. Experimentally, QCs have been found to have a local icosahedral symmetry with a spatial coherence length close to that of the silicon standards despite the absence of translational symmetry. Nonpropagating local disorder as froze tiles flip[6], tunneling states[7] or the activation of a new type of dynamics due to atomic jumps (called phasons[5]) are some of the most interesting and still not yet understood consequences. Within this context, measurements of sound velocity and attenuation in perfect icosahedral AlPdMn as a function of pressure (*i.e.* density) may provide insight into the thermodynamic stability of QCs.

Nondestructive picosecond acoustic experiments belong to the family of modern ultrafast optical methods used for about twenty years, mainly carried out to measure the mechanical and thermal properties of thin-film materials[8, 9]. A short laser pulse is split into pump and probe beams. The pump is focused on an optically absorbing film surface, whereas the probe is focused to a spot of 3 $\mu$m on the opposite one. The pump laser pulse creates a sudden and small temperature rise (1 K). The corresponding thermal stress generated by thermal expansion relaxes by launching an acoustic strain field. After propagation along the sample, both thermal and acoustic effects alter the optical reflectivity of the sample in two ways: the photo-elastic effect, and the surface displacement as the acoustic echo reaches the surface. The first modification contributes to the change of both real and imaginary parts of the reflectance, whereas the second one only modifies the imaginary contribution. The variation of reflectivity as a function of time is detected through the intensity modification of the probe delayed from the pump with a different optical path length. In this study, we have adapted the optical pump-probe set-up reported in previous publications[10] in such a way that measurements of acoustic echoes in DAC be possible. Ultrashort pulses (800 nm, 100 fs) are generated by a Ti:Sapphire laser. The power in each pump and probe pulse applied to the sample are about 20 mW and 3 mW respectively. The detection is carried out by a stabilized Michelson interferometer which allows the determination of the reflectivity imaginary part change[11]. Extracted from a large single quasicrystal of icosahedral $Al_{68.2}Pd_{22.8}Mn_9$ ($\rho$=5.08(1) g.cm$^{-3}$) [12] previously used to determine accurate equation of state from both ultrasonics and X-ray diffraction techniques[13], a thin platelet was loaded into the experimental volume of a DAC. Two experimental runs have been carried out with sample embedded in different PTM [14], neon and argon (see Fig. 1). Surprisingly, we systematically observed a small amount of rare gas (thickness of about 1 $\mu$m) between the anvil and the pump-side AlPdMn surface. Using the well known acoustic velocity of AlPdMn at ambient conditions[13], the thickness of the single-grain was measured to be 9.12(1) $\mu$m from picosecond measurement. Pressure was measured using the fluorescence emission of a ruby sphere [15] placed close to the sample in the gasket hole. The accuracy was better than 0.3 GPa at the maximum pressure reached.

At each pressure, two longitudinal acoustic echoes were systematically observed in the relative variation of the reflectance imaginary part. The first echo corresponds to a single way between the two surfaces of the sample, the second echo to a pulse being twice reflected back at the AlPdMn/PTM interfaces. As can be seen in Fig. 1, the acoustic signal is superimposed on a slow background variation caused by thermal effect plus a damped oscillatory component. This last contribution arises from the acousto-optic modulation of the probe beam from the acoustic waves propagating in the PTM. It has thus been treated as usually done for stimulated Brillouin scattering signals [8] in order to extract both velocity and attenuation in the PTM (neon or argon). We obtain a pres-

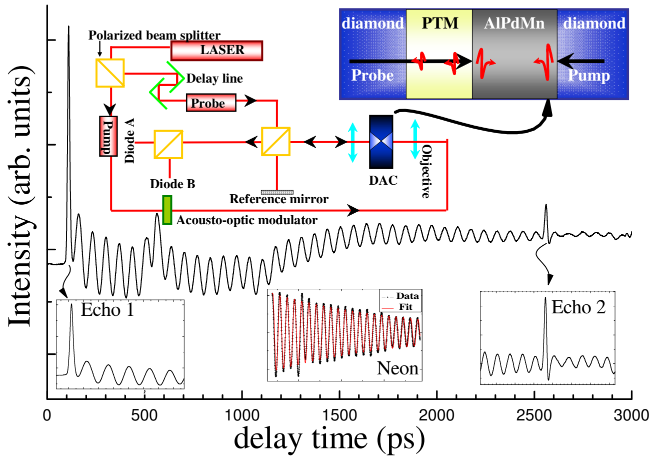


FIG. 1: Change in the reflectivity imaginary part of AlPdMn at 9.7 GPa as a function of the optical probe-pulse time delay. Up: experimental apparatus used to perform picosecond-laser acoustics studies at high pressure. The arrow indicates the schematic illustration of generation and detection process for AlPdMn in DAC. Insets : left: enlarged part of the first acoustic echo. Center: Brillouin interferences between the probe beam and the acoustic wave in the PTM where the thermal background has been subtracted. The red line corresponds to the data fit carried out to determine the attenuation. Right: enlarged part of the second acoustic echo.

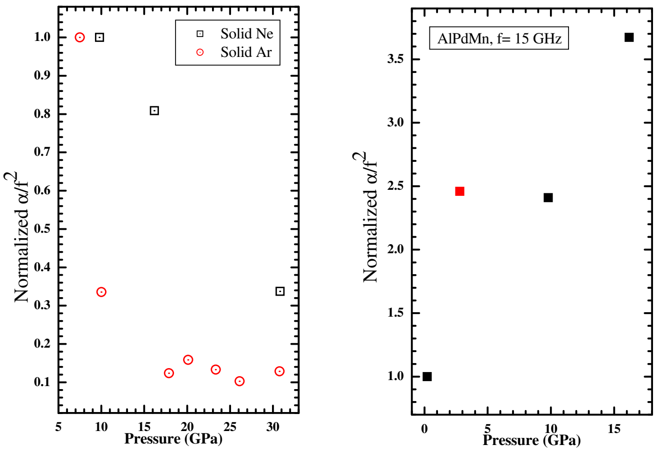


FIG. 2: Pressure dependence of the longitudinal attenuation coefficient divided by the square of frequency and normalized by the first measured point ($P_i$). Left: neon ($P_i$ = 7.5 GPa) and argon ($P_i$ = 9.7 GPa). Right: AlPdMn ($P_i$ = 0.2 GPa), the black (red) full square correspond to the upstroke (downstroke) data.

sure dependence of the sound velocity in argon and neon in excellent agreement with previously reported data[17]. Results for $\alpha/f^2$, the longitudinal attenuation coefficient divided by the square of frequency, as a function of pressure are shown in Fig. 2. We observe a negative slope of the absorption vs density which, in the case of rare gases, is related to the pressure dependence of the interaction between thermal phonons and acoustic waves.

For AlPdMn, the longitudinal velocity $v_L$ has been determined using the following equation: $v_L = 2d/\Delta t$ , where $\Delta t$ is the time interval between the two adjacent acoustic echoes and $d$ the thickness of the sample deduced at high pressure from its initial value and the pressure dependence of the bulk modulus $B$ [13]. The transversal sound velocity $v_T$ is finally extracted from the same equation of state and the definition of the bulk modulus for acoustically isotropic materials: $B = \rho(v_L^2 - 4/3v_T^2)$. Pressure dependence of longitudinal and shear waves is displayed in Fig. 3. Here again, the excellent agreement with previous ultrasonic study under hydrostatic pressure up to 1 GPa demonstrates the capability of the present method. Using these results, and according to the large pressure range probed as well as the high accuracy of our technique (the travel time is determined with an error of less than 2 ps corresponding to an uncertainty on the velocity lower than 0.5 %) we propose the following non-linear curve fit of the elastic moduli (in GPa) versus pressure (in GPa): $C_{11} = 215.88 + 7.33P - 0.024P^2$, and $C_{44} = 65.6 + 2.53P - 0.010P^2$. These results demonstrate that fourth and higher order elastic moduli, known to play a major role in the vicinity of phase transition, can be readily determined using our technique.

The attenuation per unit length in AlPdMn is computed from the ratio of the first and second echo Fourier amplitude (respectively $\Delta R_1(\omega)$ and $\Delta R_2(\omega)$) [16]: $\alpha(\omega) = (2d)^{-1} ln|\Delta R_1(\omega) * r_{QP}^2/\Delta R_2(\omega)|$ with $r_{QP}$ the amplitude reflection coefficients for the phonon strain pulse at the interface between the quasicrystal and the PTM. This coefficient is dependent on the acoustic impedances $\rho v$ only and has been determined under pressure using Ref. [17, 19]. The pressure dependence of the longitudinal attenuation coefficient divided by the frequency squared (15 GHz) is compared to the rare gas results in Fig. 2.

An obvious dissimilarity between the pressure behavior of $\alpha$(P) in solid Ne (or Ar) and AlPdMn is observed. An explanation to account for such a peculiar result could be related to the interaction between phonons and dynamical defects in QCs: increasing temperature above a few hundreds degrees C is known to allow atomic jumps corresponding to the creation of structural defects that have no counterpart in periodic solids. The activation of this phason dynamics in QCs has been found to be at the origin of phase transition[20] or strong deviation from regular crystal behavior[21]. However at 300 K the phasons are undoubtedly frozen and the phonon-phason coupling hypothesis has here to be abandoned. On the other hand, the existence of small phonon-like atomic displacements due to an initial static disorder of freeze tiles flip[6] and/or the occurring of intrinsic tunneling states[7] have been invoked to be mainly *responsible* for the stability of the quasicrystalline phase at low temperature. Both effects are different from long-range atomic jump and are expected to be increased by lattice contraction. These scenarios could be an explanation for the singular behavior of pressure-induced sound absorbtion through the

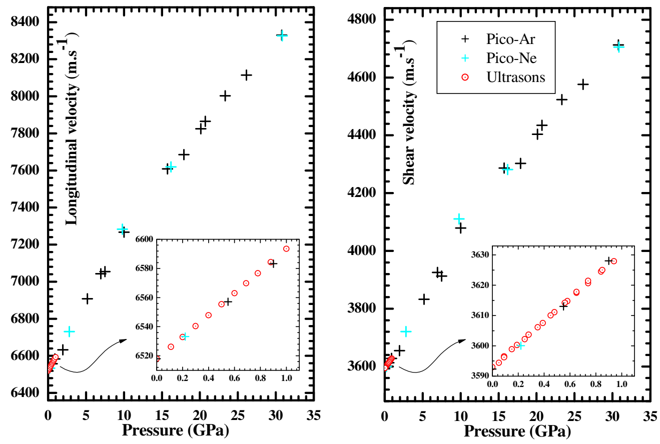


FIG. 3: Left: longitudinal sound velocity of AlPdMn as a function of pressure. Right: shear sound velocity of AlPdMn as a function of pressure. Red circles: ultrasonic data[13]. Black crosses: picosecond data from the first run using argon as PTM. Cyan crosses: picosecond data from the second run using neon as PTM. In both runs, no difference between upstroke and downstroke data was detected.

existence of a secondary elastic strain due to short-range atomic displacement (the freeze tiles flip hypothesis) or of a tunneling state-phonon coupling. The origin of relaxation in QCs at temperature lower than the phason dynamics activation is thus quite different than regular crystals, but the intrinsic mechanism should still be analytically represented through the Akhieser formalism[18]:

$$\frac{\alpha}{f^2} = \frac{2\pi^2 T C \tau}{{v_L}^3} \Gamma^2 \qquad (1)$$

where $C$ is the specific heat per unit mass of the crystal, $T$ the temperature, $\tau$ the mean lifetime of thermal excitations, and $\Gamma^2$ the visco-elastic contribution to the sound absorption. The pressure variation of $C\tau\Gamma^2$ term in AlPdMn, shown in Fig. 4, follows the same behavior as those from rare gases despite the difference on the attenuation. This is in agreement with Duquesne[22] who has demonstrated that the thermoelastic contribution to the process of sound absorption in AlPdMn is negligible in the GHz range with respect to the viscosity of the phonons gas (100 K < T < 300 K). Lattice contraction effect on the sound absorption could thus be interpreted through a peculiar Akhieser contribution due to interaction between acoustic waves and short-wavelength fluctuations. These intrinsic excitations could be invoked into the extraordinary stability of QCs versus pressure (the pressure transition of AlPdMn is higher than 80 GPa[23] and still unknown), as well as the pressure-induced phase transition from an approximant to a quasicrystal[24]. However, we point out that our interpretation should be considered as a tentative which is now addressed theoretically in order to get microscopic insight into the relaxation phenomena in phason-free QCs. This would *in*

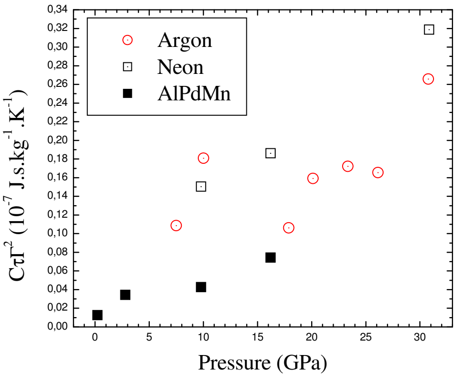


FIG. 4: Pressure dependence of the $C\tau\Gamma^2$ Akhieser term.

*fine* provide information on the quasiperiodic long-range order propagation and on the quasicrystal stability.

To conclude, we have demonstrated through the study of AlPdMn the feasibility of carrying out picosecond acoustics combined with the most versatile and powerful high pressure device, the DAC. In both cases, a small dimension of the sample is mandatory. This new high pressure tool makes possible accurate measurements of attenuation (not amenable with any other traditional techniques), and velocity of longitudinal waves in the tens of GHz range. We measured a singular behavior of pressure-induced sound attenuation in AlPdMn, which gives new experimental insight into the intrinsic effect that stabilizes the free of long-wavelength phason fluctuations quasicrystalline phase. This method can be easily extended to elastic investigations of all materials (opaque, transparent, single- or polycrystal, nanomaterials, or liquids) up to several Mbar and thousands of K. We believe that the technique of picosecond acoustics in DAC is a critical step forward to the study of elastic properties under extremes conditions. Finally, it has to be pointed out that recent works indicates a conceivable extension of the present development to the detection and generation of shear waves[25], as well as the investigation of thermal properties[26] as a function of pressure and temperature. So far, this technique is likely to have an impact on the study of dynamics of solid and liquid states at high density.

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