Low-Energy Modes in Icosahedral and Glassy $Pd_{58.8}Si_{20.6}U_{20.6}$: A Comparative Study by Neutron Inelastic Scattering

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In contrast to the strong difference observed in the static-structure factors of icosahedral and glassy Pd-Si-U, samples of their dynamical properties as reflected in their generalized vibrational density of states are nearly identical and quite different from that of the fully crystallized samples. Low-energy modes are detected in the generalized vibrational density of states of the icosahedral phase, which lead to an enhanced intensity at energies below 10 meV as compared with that of the crystallized samples. Also, the wavelength dependence of the low-energy modes in icosahedral Pd-Si-U is very similar to that in the metallic glass.

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From the three levels of order [short-range order (SRO), long-range bond orientational order, and translational invariance present in crystals] in quasicrystals[1,2] only the first two are preserved, while glasses are predominantly characterized by SRO. A consequence of these different degrees of order is the very different static structure factors observed for these three phases of condensed matter. As the dynamics of an atom strongly depends on the mutual arrangement of the surrounding atoms, i.e., on the structure, we have started to investigate the dynamical properties of quasicrystals using neutron inelastic-scattering techniques.

Here we report the results of one of several neutron inelastic-scattering experiments in which the frequency spectrum (FS) and the dynamic structure factor $S(Q,\omega)$ were determined for one set of $Pd_{58.8}Si_{20.6}U_{20.6}$ samples at room temperature. Three samples of approximately equal weight were made from 105 g of the as-quenched metallic glass. One part was measured in the as-quenched state, then the same glass after structural relaxation (30 min at 668 K) and finally after crystallization of this sample at 850 K (mixture of several polycrystalline phases, predominantly[3] UPd_3). The second part of the metallic glass was brought into the quasicrystalline state by a short annealing between 773 and 803 K. This quasicrystalline sample contained 6% to 7% still unconverted but structurally relaxed glass, and less than 1% crystallized material as determined from differential scanning calorimetry and x-ray diffraction. All samples were measured under identical experimental conditions at the cold-neutron time-focusing time-of-flight spectrometer IN6 at the high-flux reactor of the Institut Laue-Langevin in Grenoble, France. The relevant parameters of this experiment were incident energy $E_0=3.866$ meV, range of scattering angles 11° and 114° (corresponding to momentum transfers Q for elastically scattered neutrons between 3 and 25.7 nm^{-1}), and an energy resolution of the elastically scattered neutrons of $\Delta E_0=125$ μeV (FWHM).

From the measured time-of-flight spectra the double-differential scattering cross section and from this the total dynamic structure factor were calculated, applying all necessary corrections[4] except those for multiple scattering of neutrons and for the resolution function of the spectrometer. At small Q values this contribution of multiply scattered neutrons to $S(Q,\omega)$ is not negligible. However, as all samples were equally weak scatterers (7% of the incident intensity in total), the comparison of the dynamic structure factors determined in the same way remains valid. Correction for the energy-dependent finite resolution of the spectrometer would be important in the case of the time-focusing time-of-flight spectrometer IN6, if one would not restrict the discussion on the low-energy part of the spectra as is done here.

As Pd, Si, and U scatter neutrons coherently, the frequency spectra were determined from the weighted sum of all spectra[5,6] ($\sum d^2\sigma/d\Omega\, dE \sin\theta$). Multiphonon contributions to the measured intensity were subtracted in an iterative correction procedure with use of the incoherent and harmonic approximation until self-consistency was obtained. All FS are normalized to 1 with a cutoff energy of 48 meV known from the generalized vibrational density of states (GVDOS) determined with an incident energy of 59.3 meV at our thermal-neutron time-of-flight spectrometer at the reactor MELUSINE in Grenoble, France. Because of the convolution of the GVDOS with the resolution function of the spectrometer we shall call the resulting density of states (DOS) a *frequency spectrum* (FS) rather than a GVDOS.

Figure 1 shows a comparison of the FS of the

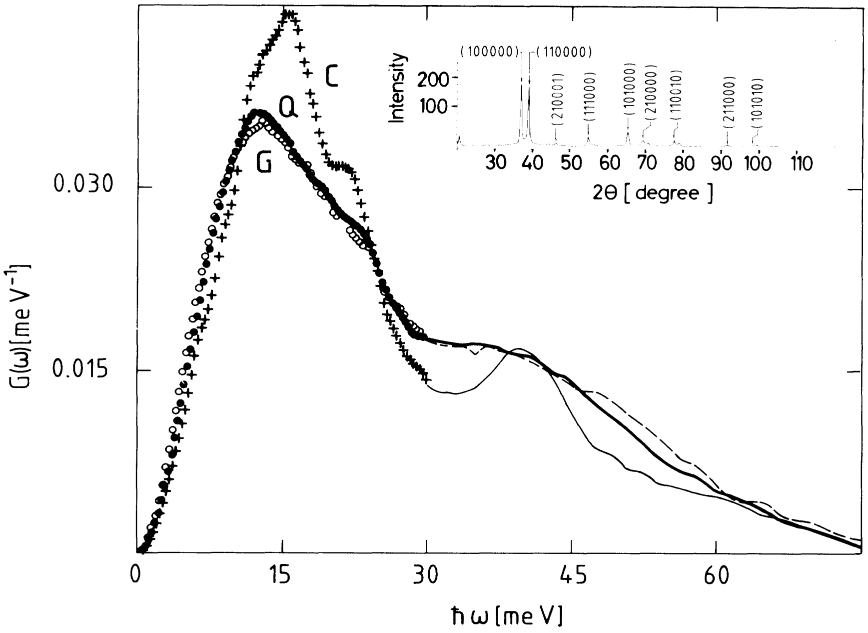

FIG. 1. Frequency spectra of as-quenched glassy (open circles and dashed line, G), isosahedral (filled circles and solid line, Q), $Pd_{58.8}Si_{20.6}U_{20.6}$ and the crystallized sample (crosses and solid line, C). A solid line was drawn through the very dense line of measured values in the energy region > 30 meV, not discussed here. The error bars for the relative accuracy between the FS are of the order of the symbols. The mean error an absolute scale as estimated from different independent measurements is 7% to 8%. Inset: X-ray diffraction pattern of the icosahedral sample. Only a few lines have been indexed to avoid overloading the inset.

icosahedral with that of the crystallized sample. The crystallized sample shows a well-structured two-band spectrum with a separation of the lower and the upper band near 28 meV and the main maxima near 15 and 26 meV. Compared with this spectrum, the FS of the icosahedral sample is very different, nearly structureless in each of the two bands, and the separating minimum is hardly seen in Fig. 1 (but is clearly seen in the GVDOS measured with thermal neutrons). The lower intensity of the high-energy band and the intensity at $\hbar\omega > 50$ meV are due to the resolution function of the spectrometer. The FS of the as-quenched glass is nearly identical to the FS of the icosahedral phase as is shown in the same comparison in Fig. 1. As for all metallic glasses, we find additional intensity at energies below 10 meV in the FS of the as-quenched glass compared with the FS of the crystallized sample which are attributed to low-energy modes (LEM), characteristic for the atomic dynamics of *disordered solids.*[7] *The same additional intensity* though reduced *is found in the FS of the icosahedral phase*, which is attributed to the same sort of LEM as exist in the metallic glass and not to phasons[8] which were expected at very low energies, but were not observed here. This can be seen more clearly in Fig. 2, where the differences of the FS are shown obtained by subtracting the FS of the crystallized sample from the FS of the icosahedral sample and from the FS of the as-quenched glass. The LEM appear as the positive part of the difference spectrum at energies below 10 meV.

The existence of LEM clearly demonstrates some disorder in icosahedral Pd-Si-U (icosahedral glass[9] or "phason strains"[10]). The lower difference spectrum of the icosahedral phase at energies below 10 meV shows that there are *less* LEM (and less disorder) in the icosahedral phase than in the as-quenched *and* in the structurally relaxed glass (even though no "degree of relaxation" can be given). It is important to recall that icosahedral Pd-Si-U is made by thermal treatment of the as-quenched metallic glass. Thus part of the lower intensity of the LEM in the difference spectrum of the icosahedral phase is due to the loss of LEM during annealing of the glass[11] and part is due to the transition to the icosahedral phase.[12] Most of the rapidly quenched-in structural properties should have been annealed out during the heat treatment and during the phase transition. We therefore conclude that the existence of LEM and the disorder related to them seems to be an inherent (and unavoidable) property of icosahedral Pd-Si-U made from the glass.

The point of view that the LEM in icosahedral and glassy Pd-Si-U have a similar origin is strongly corroborated by the wavelength dependence of these modes as obtained from $S(Q,\omega)$. Figure 3 shows cuts through the dynamic structure factors of the as-quenched glass, of

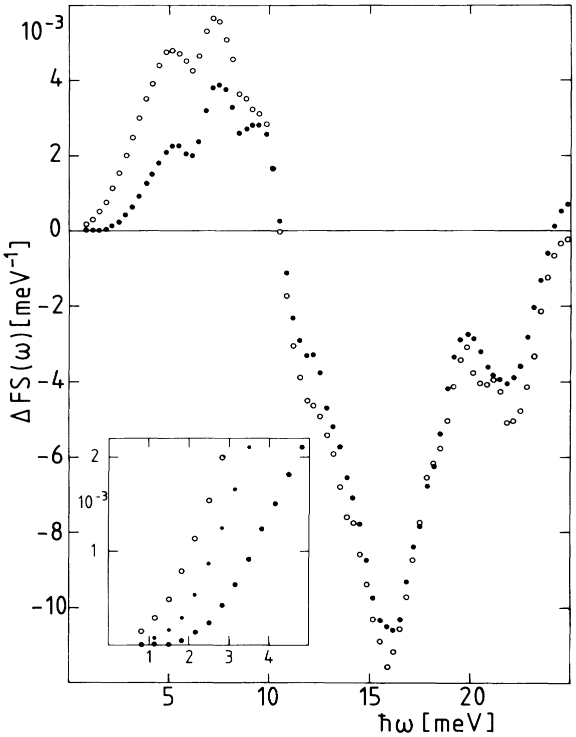

FIG. 2. Low-energy part of the difference spectra of the three FS shown in Fig. 1: $\Delta FS_G = FS$(as-quenched glass) $-$ FS(crystallized sample) (open circles), $\Delta FS_Q = FS$(icosahedral) $-$ FS(crystallized sample) (solid circles). The positive difference in favor of the glass and of the icosahedral sample gives the amount of LEM not present in the FS of the crystallized sample. The relative errors between the two ΔFS is of the order of 10%, the error on absolute scale (see above) is 30%. Inset: Augmented low-energy part of ΔFS showing the different behavior of the DOS of LEM for the as-quenched (open circles) and the annealed (small filled circles) metallic glass and icosahedral $Pd_{58.8}Si_{20.6}U_{20.6}$ (large filled circles). We find a *lower limit* of the DOS of LEM in the case of the icosahedral sample near 1.5 meV and a *higher* sensitivity of the LEM with *lowest* energy of structural annealing.

the icosahedral, and of the crystallized sample at constant energy transfers corresponding to the beginning, the middle, and the end of the DOS of the LEM in Fig. 2. While at the end of this distribution (near 10.1 meV) the cuts through $S(Q,\omega)$ run nearly parallel, and $S(Q,\omega)$ of the crystallized sample fluctuates by less than $\pm 20\%$ in the Q range covered here for *all* three ω values, the dynamic structure factor of glassy *and* of icosahedral Pd-Si-U rises by a factor of 2 for $Q > 26$ nm^{-1} in the energy range of the LEM. For metallic glasses one explanation for this rise in intensity near Q_p, the Q value at which the static structure factor $S(Q)$ attains its principal maximum, has been given in the framework of "diffuse Umklapp scattering,"[13] in which transverse modes couple to the neutrons in disordered solids outside the first Brillouin zone $(Q > Q_p/2)$.[14]

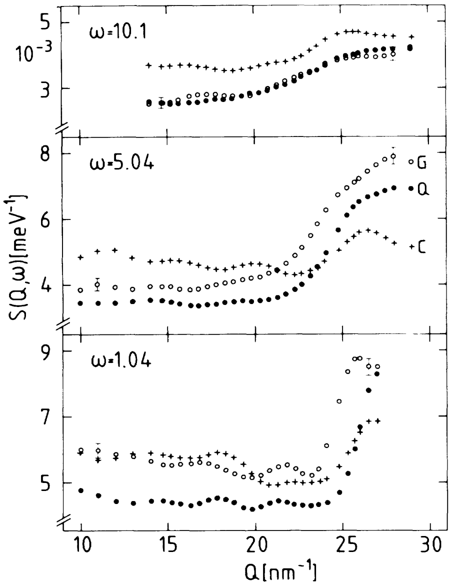

FIG. 3. Cuts through the dynamic structure factors of the as-quenched glass (open circles, G), icosahedral $Pd_{58.8}Si_{20.6}$-$U_{20.6}$ (filled circles, Q), and the crystallized sample (crosses, C) at three different energy transfers corresponding to the beginning, the middle, and the end of the DOS of the LEM. Error bars take into account statistical errors only.

From the similarity of the wavelength dependence of $S(Q,\omega)$ in the energy region of the LEM and in the Q range covered in this experiment we conclude that the same mechanism is responsible for the rise of $S(Q,\omega)$ at Q values near the (100000) and (110000) lines[3] in the static structure factor of icosahedral Pd-Si-U. This would suggest that an appreciable amount of the LEM is of transverse type also in the icosahedral phase, leading to a lower shear modulus than that of the crystallized sample. An additional contribution could be due to a nonzero minimum of a dispersion branch of collective excitations near Q_p, as has been found in several metallic glasses[6] but not yet for Pd-Si-U.

The thermodynamic consequences of the LEM are an enhanced specific heat at temperatures below 100 K. Using *just for this comparison* the FS of the different samples like normal VDOS of elements we have calculated the vibrational part of the specific heat of the different samples. Figure 4 shows that the slopes of the resulting specific heats agree well with the specific heat of icosahedral $Pd_{58.8}Si_{20.6}U_{20.6}$ measured at low temperature[15] at temperatures where the contribution of vibrations of C/T dominates.

The striking and surprising similarity of the atomic dynamics of quasicrystalline Pd-Si-U with that of the corresponding metallic glass in contrast to that of the crystallized sample as reflected in the FS and in $S(Q,\omega)$ leads us to conclude that the SRO in quasicrystalline Pd-Si-U must be similar to that in the corresponding

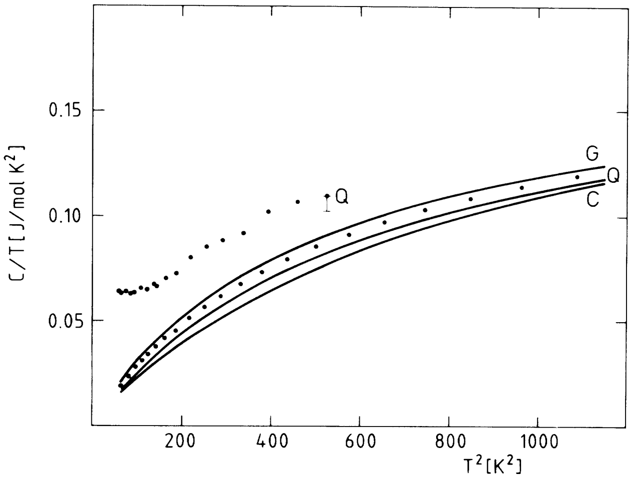

FIG. 4. Vibrational part of the specific heat divided by T calculated from the measured FS of as-quenched glassy (G), annealed glassy (points between the lines), and icosahedral (Q) $Pd_{58.8}Si_{20.6}U_{20.6}$ and of the crystallized sample (C). The dots above the curves is the measured specific heat of icosahedral (Ref. 15) $Pd_{58.8}Si_{20.6}U_{20.6}$ and includes electronic and magnetic contributions. Relative errors between the C/T curves are of the order of the symbols; the absolute error of the whole set of curves is ≤ 0.01 J/mol K^2.

glass. This view is supported by the measured pair distribution function of $Pd_{58.8}Si_{20.6}U_{20.6}$,[16] and structural relaxation observed in quasicrystals.[17] If the SRO in quasicrystalline Pd-Si-U is dominated by icosahedral symmetry our results suggest that there is also a certain amount of icosahedral symmetry in the SRO of the corresponding metallic glass.[18]

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