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Report:

**Introduction**

Quasicrystals are materials with long range order but without the lattice translation symmetry. Their atomic structure is now better understood thanks to the discovery of the binary icosahedral phase i-$YbCd_{5.7}$ in 2000 [1] which led to a detailed understanding of the atomic structure of the CdYb icosahedral phase [2]. Both the quasicrystal and its periodic approximant of cubic symmetry can be described by a quasiperiodic or periodic packing of the same atomic cluster which is made of successive shells of approximate icosahedral symmetry and contains 158 atoms. One characteristic feature of this cluster is the central Cd tetrahedron, which breaks the icosahedral symmetry of the other shells (Figure 1). It has been shown that the tetrahedron is orientally disordered in the cubic $YbCd_6$ approximant at room temperature [3] and orders below 110K, leading to a phase of lower symmetry [4]. It is believed that this central tetrahedron plays a crucial role in stabilizing the quasicrystalline long range order, it is therefore important to understand the detailed ordering mechanism and the nature of the interactions leading to this ordering.

Watanuki et al. have investigated the phase stability of the $YbCd_6$ approximant in the temperature-pressure regime up to 5.2 GPa and down to 10K. They have observed an extremely rich structure with up to five different superstructures. In particular the direction along which the ordering develops is pressure dependent (either 110 or 111). Moreover, $T_c$ increases when the pressure increases [7].

Isostructural phases have been discovered in the Sc-Zn system were the quasicrystal ZnSc and the 1/1 approximant $Zn_6Sc$ have been synthesized [5-6]. The 1/1 cubic approximant $ScZn_6$, also displays a low temperature phase transition. The structure of the low-temperature phase has been determined by synchrotron powder X-ray diffraction, showing that the Zn tetrahedra are ordered in an antiparallel fashion along the [110] direction of the high- temperature phase [6]. It is postulated that one main driving force of the phase transition is the close-packing of Zn and Sc atoms.

Recently, we obtained a millimeter size single grained $ScZn_6$ which shows a sharp phase transition at about 160K, clearly evidenced on synchrotron experiment (D2AM beam line). The purpose of the experiment was a study of the P,T phase diagram of this $Zn_6Sc$ periodic approximant..

**Exprimental data and results**

Small single grains (about 20 to 90 µm in size) were obtained by crashing a millimeter size single grain. The single grains were mounted inside the pressure cell and inserted in the cryostat for P and T studies. Three different pressure cells were used to investigate the pressure range (i) 0-4 Gpa, (ii) 0-12 GPa, (iii) 0-35 Gpa. We performed full data collections (oscillations 60° range, step 1°) attenuated and un-attenuated at various P and T, together with a small 15° range oscillation which from ambient pressure data was show efficient to pin point the phase transition (Figure 1). We have carried out the measurement at T=180K and for pressure from 0.3 to 35 Gpa. We did not observed any phase transition at this temperature up to 12 Gpa. Detailed T studies were thus carried out at 4 different pressures to determine the phase transition and check for the symmetry of the low T phase. We found that Tc varies only slightly when increasing the pressure (measurements at 0.35, 3.4, 5, 7 and 12 GPa) going from 160 to 163 K. We also found that the low T phase remains an ordered phase, with ordering along the (110) direction of the high T cubic phase and a monoclinic symmetry. A data collection was also carried out at 50K and 12 Gpa, and confirmed the stability of the monoclinic phase down to this low temperature. At 25 Gpa, we found that a new phase is appearing at 180K. This phase corresponds to a 4 time cell as shown by the 0 and 0.25 layer (in cubic symmetry) shown on the figure 1. This phase was found to be stable up to 250 K, and remains at 35 GPa. Further investigations are necessary to precisely determine the P, T domain of this new phase.

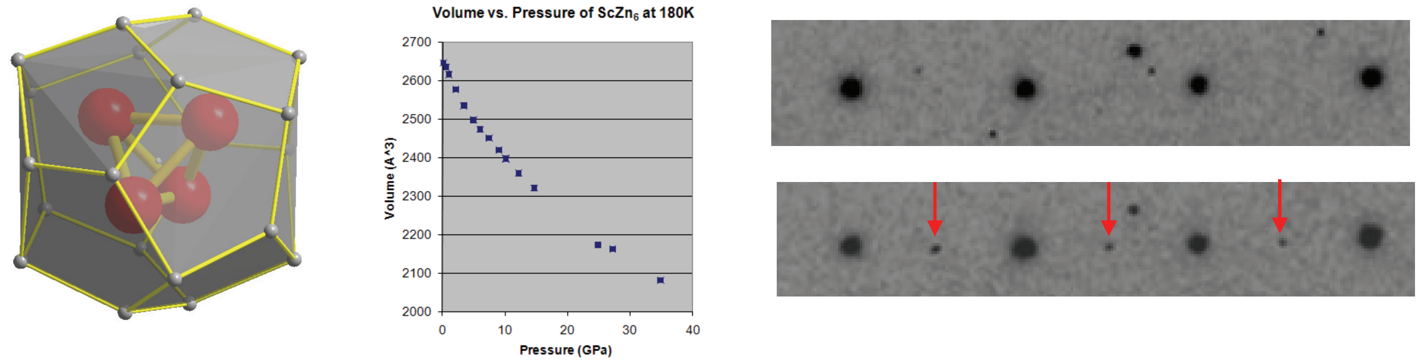


Figure: Left the central Zn tetrahedron inside the first dodecahedral shell. Centre: Pressure dependence of the unit cell volume at 180 K. Right: portion of a 15° oscillation taken at 7 Gpa at 167 K (top) and 160 K (bottom). The superstructure reflexions along (110) are indicated by red arrows, and are lying half-way between main Bragg ones.

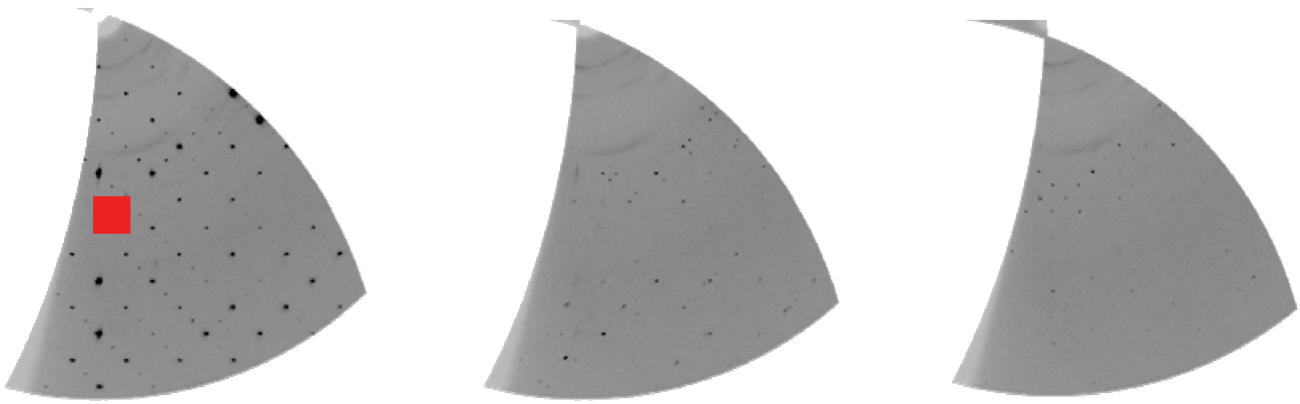

Figure: Reconstructed L=0, 0.25 and 0.5 layer of the reciprocal space as measured at 180 K and 35 GPa, where L refer to the high T cubic indices. The high temperature reciprocal cell (BCC extinction) is shown in red. Superstructure reflexions are visible on the 3 layers, demonstrating the occurrence of a new superstructure.

**References**

[1] A. P. Tsai, J. Q. Guo, E. Abe, H. Takakura and T. J. Sato, Nature 408 (2000) 537.
[2] H. Takakura, C. P. Gomez, A. Yamamoto, M. de Boissieu and A. P. Tsai, Nature Materials 6 (2007) 58.
[3] C. P. Gomez and S. Lidin, Phys. Rev. B 68 024203 (2003).
[4] R. Tamura, et al., Phy. Rev. B 72, 174211 (2005).
[5] P. C. Canfield, et al., Phy. Rev. B 81, 020201R (2010)
[6] T. Ishimasa, Y. Kasano, A. Tachibana, et al., Phil. Mag. 87 (18-21): 2887-2897 (2007).
[7] T. Watanuki, et al., Phy. Rev. Lett. **96,** 105702 (2006)