ESRF	**Experiment title:** Inelastic X-ray Scattering Study of Chain Melting in Incommensurate Rb-IV	**Experiment number**: HS-2898
Beamline: ID28	**Date of experiment**: from: 25/11/2005 to: 3/12/2005	**Date of report**: 25/02/07
Shifts: 18	**Local contact(s)**: A. Bossak	*Received at ESRF:*

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Report: Over the past 5 years we have discovered an entirely new class of incommensurate crystal structures in Rb, K, Sr, Ba, Sb, Bi, As and Sc at high pressure [1,2]. These composite "host-guest" structures comprise a tetragonal host structure with octagonal channels along the *c*-axis which contain 1-dimensional chains of guest atoms, which are incommensurate with the host structure along *c*. The composite structure of Rb-IV is different from that of Sr, Ba, Sb, Bi, As and Sc, and is currently unique amongst the elements [1,2]. Rb-IV is also unique in exhibiting a pressure-induced phase transition at P_c=16.7GPa on pressure decrease from a composite structure where the guest chains have long range order to a phase where both inter- and intra-chain ordering is lost, leading to a crystalline host structure containing 1D liquid-like chains [3,4]. The diffraction patterns from high-quality single crystals of Rb-IV reveal both Bragg spots from the crystalline host lattice, and intense sheets of diffuse scattering from the "melted" liquid-like chains.

While the melted chain state was previously unknown in an element, a similar incommensurate structure with liquid-like chains has long been known in $Hg_{3-\delta}AsF_6$ at ambient pressure, where inelastic neutron scattering studies of the disordered chain state have determined the 1-dimensional (1-D) longitudinal acoustic phonon dispersion curve associated with the randomly phased chains of Hg atoms, and the 3D phonons from the host lattice. We wished to perform a similar study of Rb-IV – to determine the phonon dispersion curve of the 3-D host lattice and the 1-D in the ordered chain phase at 300K, and determining the phonon dispersion spectrum associated with the disordered chains of guest atoms. *These would be the first inelastic scattering studies of any of these unique host-guest structures.* **In this experiment we asked for 6 days of beamtime on ID28 to measure the 3D phonon dispersion of the host lattice and the 1D dispersion of the guest chains of the incommensurate host-guest structure of Rb-IV.**

Scattering data were collected from two high-quality single crystals of Rb-IV. One crystal was investigated at a pressure of 18.4GPa, while the second was studied at 17.3, 17.0, and 16.3GPa. The scattering geometry is shown in Fig. 1. Figure 2 shows selected IXS spectra recorded from the second crystal of Rb-IV at 17.3GPa for three different momentum transfers Q. Despite the smallness of the sample in the pressure cell (scattering volume ~2×10^{-5} mm^3), high-quality spectra were obtained in ~90mins. The spectra exhibit a clear Q-dependence, and comprise one or two inelastic features of varying energy and intensity in addition to the elastic line. From the decompositions of the measured IXS spectra, the longitudinal phonon energies were obtained as a function of momentum transfer (Fig. 3). The data points clearly separate into two dispersion branches. The first (solid symbols) exhibits the periodicity of the host lattice along the *c* direction. The apparent doubling of the periodicity originates from the body-centered nature of the host lattice. The second E(q) data set (open symbols) has a minimum at $(0\ 0\ 3.27)_h$ in the reciprocal lattice of the host, which corresponds to the $(0\ 0\ 2)_g$ lattice point of the guest structure. We thus observe two two dispersion branches with the periodicity of the host and the guest lattice, respectively. They are thus assigned to separate LA-type

phonon branches of the host and the guest sublattices, as one would expect in an idealized composite system without host-guest interaction.

The effective sound velocities in the host and guest structures were determined from the initial slopes of the fitted phonon dispersion relations (Fig. 3). The host and guest sound velocities are equal at a pressure of 18GPa (v =3800(100) m/s), and they differ by less than 10% throughout the pressure range studied. The sound velocities determined for the guest chains are approximately 10% lower than we estimated recently from diffuse X-ray scattering measurements at ESRF [4]. The speed of sound in the guest chains increases linearly at a rate of 280(80) m/sGPa−1, and the present data show no evidence of any change in the sound velocity along the chains below 16.7GPa, the pressure at which the inter-chain correlation length begins to decrease rapidly [3,4]. More detailed studies at a greater number of pressures would be needed to address this question definitively.

In summary, we have made the first experimental investigation of the lattice dynamics in an element with an incommensurate composite structure. Two well-defined LA-type phonon branches are observed in Rb-IV along the direction of the incommensurate wavevector, which are assigned to separate LA-type phonons of the host and the guest sublattices. The success of these measurements open the way to further detailed studies of the dynamics of these unique structures in the future, including studies of chain disorder and intra-phase transitions.

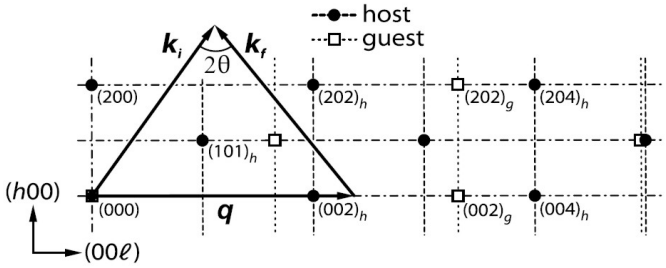

Fig 1: The IXS scattering geometry. The circles and squares indicate the Bragg reflections from the host and guest lattices, respectively, $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$ are the incoming and scattered photon wave vectors, and $\boldsymbol{q}$ denotes momentum transfer vector.

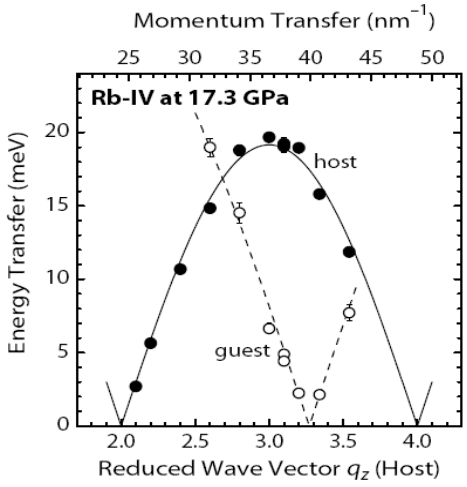

Fig 3: Dispersion relations of longitudinal lattice excitations in Rb-IV at 17.3GPa. The reduced wave vector q_z refers to the reciprocal lattice of the host, with a periodicity of c_h = 5.1527Å along the c direction. The two branches are attributed to lattice excitations of the host (solid symbols) and the guest (open symbols), respectively.

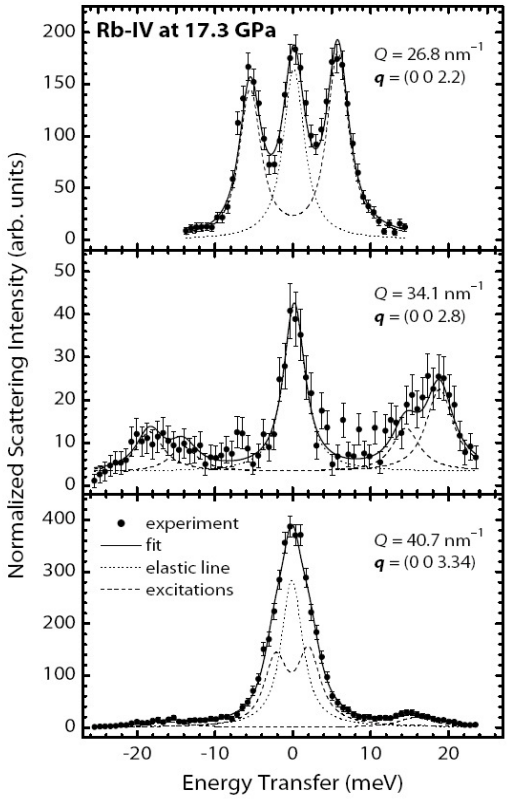

Fig 2: Inelastic X-ray scattering spectra of Rb-IV at 17.3GPa. Spectra were recorded at different momentum transfers Q. The reduced wave vector q refers to the reciprocal lattice of the host, with a periodicity of c_h=5.1527Å along the c direction.

References:

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