Summary

The surface of a crystal is the place where the crystal interacts with its environment. Knowledge of the atomic structure of a solid-liquid interface is important to understand the different processes occurring at the surface, such as crystal growth. Both the structure at the solid side and on the liquid side of the interface deviate from the bulk structure. The crystal surface can show relaxations and even a reconstruction of the outermost surface layer. The liquid at the surface 'feels' the periodic potential of the crystal and can adopt some of its ordering. In this thesis two different kind of solid-liquid interfaces have been investigated, ionic crystals in water and molten metal monolayers on a germanium crystal.

The first two chapters describe the interface structure of KDP and KBC crystals in their growth environment. In chapter 2 we have used surface x-ray diffraction to determine the atomic structure of the liquid at the KDP/water interface using ultra-thin water layers. These ultra-thin layers were obtained using a specially developed 'environment cell' in which the relative humidity is 100% and the temperature can be controlled. The water layer thickness increases with increasing relative humidity and temperature (i.e. with increasing water vapor pressure).

The liquid structure at the interface shows two important features. First, at all conditions measured the crystal is covered with two ice-like layers of water molecules that are tightly bound to the surface and occupy well defined positions on the surface. Second, these ice-like layers are covered by a diffuse water layer in which the first layer of water molecules still shows some ordering. The highly ordered first two water layers were unexpected for this crystal in contact with its growth solution. These layers must arise from the strong interactions with the ionic surface and deserve further theoretical investigation.

Chapter 3 describes the surface structure of KBC crystals in an humid environment. Both the (001) and (00$\bar{1}$) faces are investigated. On both faces an etch-resistant layer develops, which is shown to be amorphous. The interface between the etch-resistant layer and the bulk KBC crystal is strongly influenced by the relative humidity. This indicates that water molecules can

penetrate through this layer. The interface is atomically flat and shows no reconstructions. The crystal is terminated in an A termination, of which the outermost molecules are most sensitive to the relative humidity: at 40% RH they show an expansion and at 100% they are compressed. The measurements performed on the $(00\overline{1})$ face suggest a different atomic structure of this face, which gives some more insight in the hypomorphism found for the KBC crystals.

Liquid metal monolayers on a Ge(111) surface are described in chapters 4, 6 and 5. In chapter 4 the Sn/Ge(111) system is discussed. At higher temperatures the Sn layer is molten. The structure of the molten Sn-layer has been determined at different temperatures with SXRD experiments. Our analysis shows that the liquid Sn exists as a dynamic, 2D-layer with Sn atoms residing preferentially on sites imposed by the Ge(111) lattice. The structure of the liquid Sn layer gradually changes with temperature from more solid-like to more liquid-like. The most important change is the decrease of the percentage of Sn atoms near lattice sites at higher temperatures. The question arises whether this behavior changes if the liquid layer changes from 2-dimensional to 3-dimensional. Unfortunately, the Sn/Ge(111) system is not suitable to investigate this, because the Sn layer does not completely wet the Ge surface at higher coverage.

The Pb/Ge(111) system is investigated in the last two chapters. The structure of the low-temperature phase is discussed in chapter 5 while the nature of the melting transition is described in chapter 6. We have shown that at a nominal coverage of $\frac{4}{3}$ ML two different $\sqrt{3}$ structures exist, the β and β' structure, which combine small structural differences with a large difference in transition temperature and melting behavior. The different melting behavior of the two phases can be explained by the bulk Pb atoms on the surface. On the β' surface, the excess Pb is distributed evenly on the surface in small islands. Each Ge(111) terrace is in direct contact with a bulk Pb island, and these islands act as a vacancy sink, inhibiting the β' structure from melting until the bulk melting point is reached. After cooling, the excess Pb is arranged in bigger islands that do not influence the melting behavior of the β phase. A microscopic technique (e.g. STM or LEEM) is necessary to confirm our hypothesis for the behavior of the excess Pb.

The critical exponents of the 2D phase transition of the β phase correspond to the values expected for mean field behavior. This indicates that the Pb atoms have long range interaction potentials.