

planes parallel to the surface. With q being the charge per unit area and A being the unit cell area in a distance larger than a few lattice spacings the potential of such a plane is of the form

$$V(z) = -\frac{1}{2\epsilon_0} \frac{q}{A} |z|$$

The potential is identical to the one of an infinitely extended charged plate with charge density $\sigma = \frac{q}{A}$.

The corresponding electrical field is simply

$$E(z) = \frac{1}{2\epsilon_0} \frac{q}{A}$$

Consider now Fig. 1.23(a). Each plane has an overall zero charge due to the cancellation of the charges of the two sublattices.

Additional planes on the crystal surface do not contribute to the energy of the ions in the bulk, as their potential at the ions location is zero. There is no effect of the surface on the Madelung energy of bulk ions.

Consider Fig. 1.23(b). Though charged, the planes in the repeat unit are symmetric and the repeat unit is neutral without a dipole moment.

The potential of each repeat unit at a distance z a few repeat unit distances away from it is zero. Thus, there is no surface effect on the Madelung energy of bulk ions.

Consider now Fig. 1.23(c). Though the repeat unit is neutral, it has a dipole moment. The potential of the repeat unit at large distances is of magnitude

$$V = \frac{1}{2\epsilon_0} \frac{|q|}{A} a$$

Thus each repeat unit till the surface adds to the potential of a bulk ion and thus its potential energy. The Madelung energy of the bulk ions increases with crystal thickness.

If we define the surface energy as

$$\text{Surface Energy } E_s = (\text{cohesive energy of finite crystal}) - (\text{number of atoms}) \times (\text{cohesive per atom in finite crystal})$$

For case c) of Fig. 1.23 the surface energy diverges with increasing crystal size. We can also see directly that for an ion in the crystal the surface contributes a nonzero field. Consider plane 1 in (c). The fields of planes 2 cancel by symmetry and the dipole layers 3 and 4 create no field at plane 1 (their constant fields cancel). But the positively charged surface layer does! The constant field will give rise to a nonzero potential within the entire crystal. Another way of phrasing our result is to state that whenever there is a nonzero dipole moment in the repeat unit normal to the surface the surface energy diverges.

Such surfaces are polar surfaces.

As shown in Fig. 1.23 (d) partial charges could compensate for the problem of polar surfaces resulting in zero fields.

Experimentally we observe faceting polar surfaces, as for MgO (111) which forms MgO (100) facets (Fig 1.24)

The same kind of faceting takes place during the growth of polar surfaces as shown for EuO (111) in Fig 1.25.

If stable, polar surfaces need to redistribute charge, either electronically as shown in Fig. 1.26 or by surface reconstruction as shown for the example of NiO (111) [Fig. 1.27]. Finally also adsorption may stabilize polar surfaces by creating partial charges as in Fig 1.23 (d). Under ambient conditions dissociated water is often of relevance.

Microscopy allows also surface structure determination. However, it is often less precise and connected with a higher effort. Microscopy will be discussed in a separate chapter. By far the most popular and important method for surface structure determination is low energy electron diffraction (LEED). Fundamental to the application of low energy electrons for surface analysis is their short mean free path as displayed in Fig. 1.28. This has a number of consequences for using them as a surface probe:

- 1.) A surface bombarded with e^- emits electromagnetic radiation. Due to the short mean free path the radiation stems from the surface near layers.
- 2.) A surface bombarded with e^- emits particles (atoms, molecules) which stem from the surface.
- 3.) A solid stimulated with sufficient energy non-electronically (by X-rays, energetic atoms, ...) emits electrons. Due to their small mean free path they possess a small escape depth. The electrons are thus surface specific.
- 4.) A surface bombarded with electrons emits electrons. These electrons stem from the surface near layers. A characteristic electron spectrum is shown in Fig. 1.29.

The spectrum displays the following characteristic features:

- at low energies the peak of the true secondary electrons, which result from inelastic collisions of the primary e^- .
- the smooth background with small peaks, which either do not move with the primary energy variation, or do move. The first are Auger electrons and element specific (\rightarrow AES), the latter are due to characteristic losses of the primary e^- (e.g. plasmon losses).

- Very close to the elastic peak low peaks characteristic for small energy losses ($< 1\text{eV}$) are present. They result e.g. from the interaction of electrons with phonons or molecule vibration modes and are the basis of high resolution electron energy loss spectroscopy (HREELS)
- Finally the elastic peak of electrons which did not suffer inelastic losses. They allow the determination of surface structure as they interfere with the periodic arrangement of surface atoms.

A LEED system is schematically sketched in Fig. 1.30. Electrons are extracted from a thermal emitter and focused onto the sample into a spot of the order of 1mm diameter. The diffracted e^- pass a number of grids and are finally accelerated onto a fluorescent screen allowing to see the diffraction pattern. The first grid is on ground potential to ensure field free electron motion, the second grid (or second and third) allow to reject inelastically scattered e^- through a retarding voltage. Today, LEED patterns are usually imaged with a camera and stored digitally for quantitative analysis, e.g. of spot intensity as a function of primary energy.

For a 2D-lattice the diffraction condition reduces to

$$\vec{k}_{||} - \vec{k}_{0||} = \vec{G}_{hk}$$

where $\vec{k}_{0||}$ is the wavevector component parallel to the surface of the incident e^- , $\vec{k}_{||}$ the one of the exiting e^- and \vec{G}_{hk} a reciprocal 2D lattice vector with $\vec{G}_{hk} = h\vec{a}_1^* + k\vec{a}_2^*$. This has already been derived in the Festkörperphysik I lecture, see Script page 51.

For applying the Ewald construction, instead of reciprocal lattice points we have to consider reciprocal lattice rods normal to the surface. In the usual geometry of LEED $\vec{k}_{o||} = 0$. Ewald construction then becomes very simple: $\vec{k}_{||} = \vec{G}_{hk}$. LEED visualizes the 2D reciprocal lattice. (see Fig. 1.31)

A low background and sharp LEED spots indicate a well ordered periodic surface. Poorly ordered surfaces result in broad spots and high background intensity, no spots are characteristic for amorphous sample surfaces.

The simplest case of LEED pattern is a 1×1 truncated bulk structure as e.g. observed for Pt (111), Ni (001) etc.

Note however, that a relaxation or a chemical inhomogeneity will not be reflected in the LEED pattern.

If a superstructure forms, e.g. due to adsorption, besides the main spots of the substrate superstructure or extra spots form.

Given the known main spots in LEED and the corresponding real space lattice, one of the key tasks is to determine from the observed reciprocal superstructure spots the real space superstructure unit cell. To this end we note that

$$\begin{aligned}\vec{b}_1^* &= U_{11}^* \vec{a}_1^* + U_{12}^* \vec{a}_2^* \\ \vec{b}_2^* &= U_{21}^* \vec{a}_1^* + U_{22}^* \vec{a}_2^*\end{aligned}$$

The reciprocal space matrix U^* is related to the real space matrix U by

$$U^* = (U^{-1})^T \quad \text{or} \quad U = (U^{*-1})^T$$

$$U_{11} = \frac{U_{22}^*}{\det U^*} \quad U_{12} = -\frac{U_{21}^*}{\det U^*}$$

$$U_{21} = -\frac{U_{12}^*}{\det U^*} \quad U_{22} = \frac{U_{11}^*}{\det U^*}$$