Computation of surface states on bcc transition metals
by Mizuho Kawajiri

A thesis submitted in partial fulfillment of the requirement for the degree of DOCTOR OF PHILOSOPHY in Physics
Montana State University

Abstract:
The resolvent method Is combined with a tight-binding model in order to obtain layer-by-layer densities of states at low index surfaces of semi-infinite bcc transition metals. Shockley-type localized surface states or resonances are found in all hybridization gaps in the three symmetry directions studied. Prominent structures in the angle-resolved polarization dependent photoemission spectra are discussed in the light of the present calculation. in assigning peaks of an observed EDC to calculated initial state features, a knowledge of the final state symmetry and selection rules is extremely important.

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ABSTRACT

The resolvent method is combined with a tight-binding model in order to obtain layer-by-layer densities of states at low index surfaces of semi-infinite bcc transition metals. Shockley-type localized surface states or resonances are found in all hybridization gaps in the three symmetry directions studied. Prominent structures in the angle-resolved polarization dependent photoemission spectra are discussed in the light of the present calculation. In assigning peaks of an observed EDC to calculated initial state features, a knowledge of the final state symmetry and selection rules is extremely important.

I. INTRODUCTION

The translation symmetry of crystals facilitates the theory of solid state physics. Thus solid state physics is largely devoted to the study of electrons in the bulk crystal of ring topology ignoring surfaces. However, in practice there are many phenomena which are entirely determined by the interaction of surface atoms with atoms impinging on the crystals such as heterogeneous catalysis in which the role of d-electrons of transition metals is important, semiconductor devices or corrosion. The first step toward the microscopic understanding of such surface complexes is the study of static electron distribution at the surface both in energy and in space.

When the surface is introduced the translation symmetry of the crystal is broken and surface bonds are disrupted; these are known as dangling bonds[1]. The surface relaxes either inward or outward. Due to these changes the electrons near the surface are redistributed spatially. Rather artificial states provided by only breaking the bonds are called Shockley states[2]. On the other hand if surface relaxation and charge redistribution are considered the corresponding electron states are called Tamm States[3].

There are rather well-established common features associated with surface states which are convenient to know before attempting to perform more detailed analysis[4]. First of all, a dangling bond picture of the LCAO type works for transition metals. If bulk electron states

stick sharply out of the surface then a prominent surface effect is expected. Secondly surface states show up in absolute gaps in the bulk energy bands just as in the impurity problem in semiconductors. If the gap is too narrow a well localized surface state won't be formed but it becomes a resonance. A relative gap is an energy region where the initial density of states of a given symmetry suddenly becomes much lower but does not go strictly to zero. Such a gap may be caused, for example, by an 's'-shaped band(Fig. 1-a). What is not meant by a relative gap is a gap between bands of one symmetry embedded in a continuum due to a band of different symmetry. Such a gap would be called absolute, since we are concerned only with one symmetry type at once(Fig.1-b).

In this thesis surface density of states(SDOS) of Shockley type for normal photoemission from low index faces (001), (110) and (111) of clean Mo and W are calculated. The point where the parallel component of crystal momentum $k_{\parallel}=0$ is the most interesting point in the entire two dimensional Brillouin zone. The high symmetry at such a point removes unnecessary complication, and group theory becomes a powerful tool for the assignment of surface band structure[5].

In the following section a history of both experiments and theory related to this subject is outlined. Angle Resolved Photoemission Spectroscopy (ARPS) with the synchrotron radiation source is the best tool to probe energy band structure of electrons in the crystal[6,7].

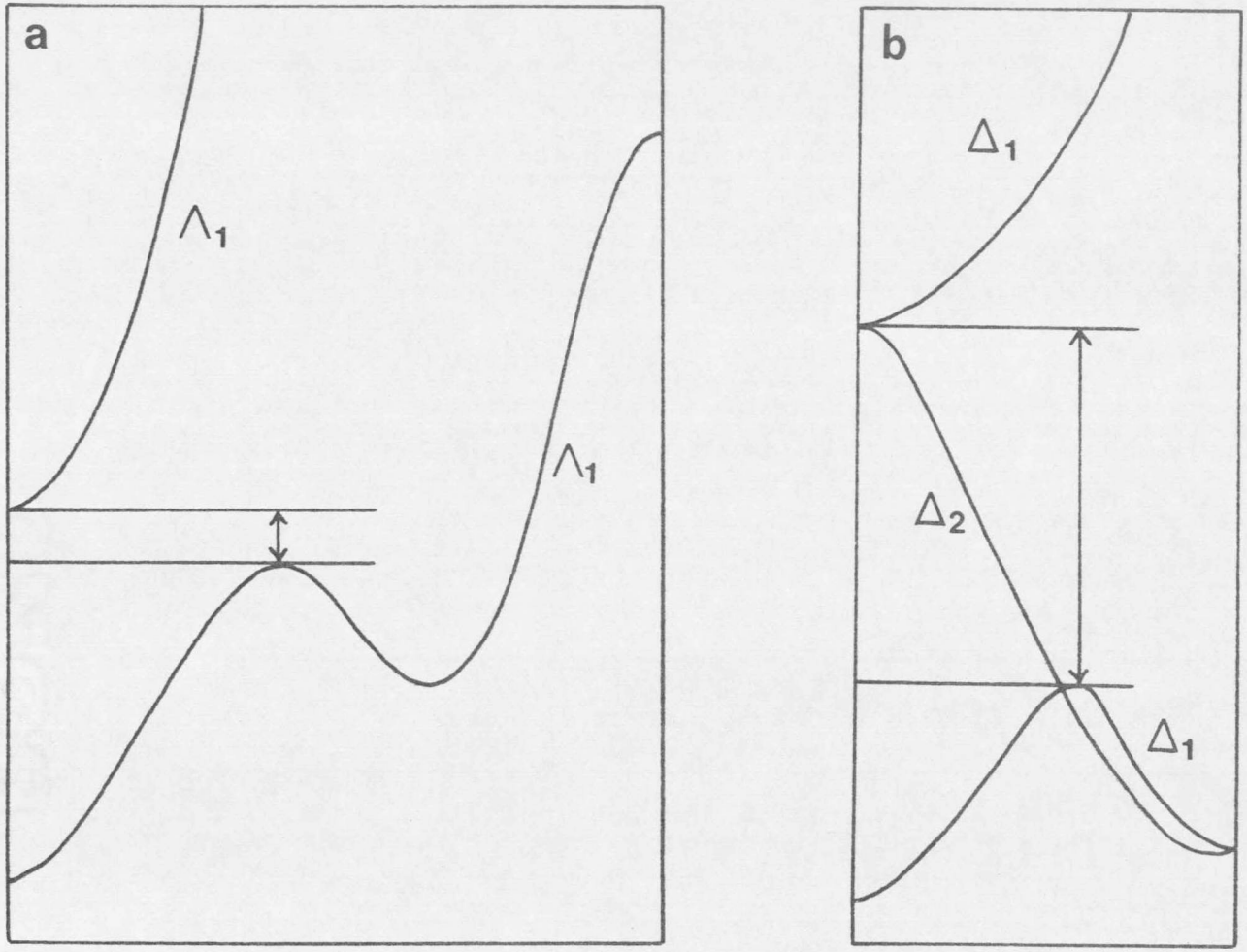

Figure 1. Relative gap (a) and absolute gap (b).

In Chapter II we look at the experiment and try to see the types of information obtained and how to relate experimental data with theory. The method of calculation is outlined in Chapter III. The results of the calculation and interpretation of the results in comparison with experiments and the possible experiments which would test the interpretation are topics of Chapter IV. Three immediate extensions using the same technique i.e. 1) application to fcc metals 2) $\bar{k}\neq 0$ calculation and 3) the chemisorption problem, are discussed in Chapter V. The details of computational problems are given in the Appendix.

A. Previous Studies of W and Mo Low Index Faces

(001) face. The existence of surface states was predicted as early as the 1930s[2,3]. More recently, Forstman, Pendry and Heine[8-11] presented a calculation of surface states in the spd hybridization gap. A sharp peak located just below the Fermi level was first observed in field emission energy distribution spectra (FEED) of W(001) by Swanson and Crouser[12,13]. Plummer and Gadzuk[14] found that this sharp peak at .4eV and another at 1.5eV below the Fermi level (E_F) were extremely senstive to surface contamination and assigned the origin of these peaks to surface states resulting from spin-orbit split bands. Feder and Sturm[15] performed a Green function type calculation based on the fact that the spin-orbit coupling mixes states of symmetry Δ_2, Δ'_2 and Δ_5

and produces one relative gap and one absolute gap between three d bands of Δ_7 symmetry. Their numerical results reveal a very pronounced surface resonance in the relative gap 0.4eV below E_F and a surface state in the absolute gap 1.5eV below E_F.

The surface sensitive Fermi peak at 0.4eV below E_F also has been observed in photoemission spectra but not the second peak 1.5eV below E_F[16,17]. The measurements of the momentum of emitted electrons as well as their energy provided a clear picture of the electron energy band structure. Feuerbacher and his co-workers[18,19] collected normal emission data from W to compare with the band calculations. The strong polarization dependence[19,7] (Fig.2) and the intensity as a function of $k_{\parallel}$[20,7] (Fig.3) of this Fermi peak were also studied. The ARPS technique has been improved considerably with the use of synchrotron radiation as the photon source, where due to the continuum nature and well-defined polarization properties of synchrotron radiation, 1) photon energy, 2) optical polarization and 3) the momentum of emitted electrons are under the control of the experimenter[7,21-23].

Contrary to the earlier interpretation[14-16] which is still the prevailing view, in particular among experimentalists, regarding the physical origin of the Fermi peak, Kasowski[24] has shown on the basis of a linear combination of muffin tin orbitals (LCMTO) technique

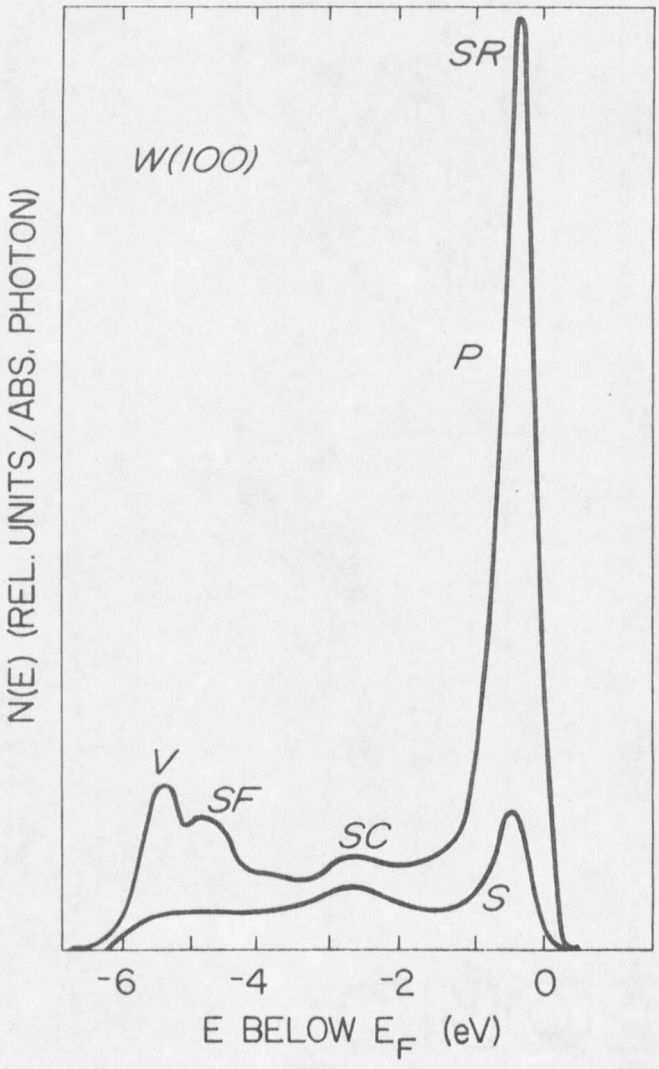

Figure 2. EDC emitted normal to the (001) face of tungsten at 10.2eV photon energy. Upper curve, p-polarized light; lower curve, s-polarized light (reproduced from Ref. 19).