Electrons in and close to correlated systems
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Chapter IV

The use of the Waveguide Principle in the Study of Elementary Excitations

Abstract:
Constant kinetic energy features resulting from surface electron waveguide behaviour are observed in low primary energy excited electron energy loss spectra on a variety of non-metallic single crystalline surfaces, among which NiO(100). Energy loss spectra on NiO with its rich $d$-$d$ exciton structure inside the conduction gap, have been studied in detail. The dependences on primary energy and scattering angles of the (surface) excitons have been studied, as well as possible resonant effects in the primary energy dependence of the surface optical phonon intensity distribution. The use of the momentum dependent surface electron waveguide conditions to enhance the features of interest in studies on constant energy loss processes, like surface phonons and (surface) inner-gap $d$-$d$ excitons is discussed.
IV. A Introduction

Secondary electrons that fulfill surface electron waveguide conditions have been proposed as the origin of constant kinetic energy features in electron energy loss and photoemission spectra on insulating surfaces in Chapter III. Electrons Bragg diffracted[1] parallel to the surface can not escape from a slab just outside the crystal as the energy corresponding to the remaining wavevector component perpendicular to the surface is too small to conquer the surface potential barrier[2]. The individual scattering processes in this region outside but close to the surface, change the phase of the electron wavefunctions. At selective momentum dependent conditions surface states can appear as a result of interference effects and confinement in image-potential derived surface states. The latter effect formed one of the main points in the original scenario but has been discussed[3, 4] to be of minor importance. Theoretical models based on the interference of the individual scattering processes, can describe extrema in elastic scattering intensities observed as a function of primary energy and/or scattering geometry. The inclusion of image-potential induced surface states slightly changes the characteristic energies and resonant shapes. Confinement in image-potential derived surface states under emergent conditions has however been concluded from recent experiments on Ag[5].

Several experimental techniques have been used to study the pre-emergent Bragg scattering induced (fine structure) effects. A variety of spectroscopic fingerprints have been reported on predominantly metallic surfaces. Interesting questions arise in the case of surface waveguide behaviour on crystals with an electronic structure determined by electron correlation effects. Is the waveguide process dependent on the surface electronic structure? The region of electron confinement is situated outside the sample and allows 2-dimensional free electron like behaviour parallel to the surface, so no direct dependence seems to be expected. However, in the case of inelastic electron injection surface and bulk electronic excitations are a prerequisite. This makes the influence of the (surface) electronic structure on the waveguide process an interesting point of study. Another aspect is the question that when enhancement of loss processes is found, is it restricted to excitations of which the induced fields extend into vacuum, like surface optical phonons[6], or do also localised excitations like the inner-gap excitons show resonant behaviour? Interference or interaction effects can in this way be selected to appear only in the slab outside the crystal or even more interesting also in the surface layers.

Whereas the previous Chapter concentrated on waveguide related results obtained on Sr$_2$CuO$_2$Cl$_2$ while briefly mentioning the results on NiO and WSe$_2$, in this Chapter the low primary energy Electron Energy Loss Spectroscopy results on in-situ cleaved single crystalline NiO will be discussed in detail. The electronic configuration of the ground state of this system is Ni$^{2+}$3$d^8$O$^{2-}$2$p^6$. As the $d$ band is only partly filled band structure calculations predict that NiO is
a metallic system. As discussed in Chapter II the correlation effects determine the low energy electronic structure and result in the insulating character of the material. Due to the large on-site repulsion $U \approx 8$ eV the lowest energy optical allowed excitation that can be made in the bulk of NiO is $3d^8 \rightarrow 3d^9 L$, where $L$ denotes a hole in the oxygen(ligand) $2p$ electron band. The excitation energy of this charge transfer process is mainly determined by the charge transfer energy $\Delta[7]$, as will be discussed in Chapter VI. The crossing of the conduction gap is however not the lowest energy electronic excitation of this monoxide. Like other transition metal oxides, for instance MnO and CoO, strongly localized inner gap $d$-$d$ excitonic excitations can be made, giving rise to weak and narrow features in or near the conduction gap region.

The electronic structure of nickel-oxygen systems contains a number of aspects that can be studied with energy loss spectroscopy. As a result a large number of reflection EELS experiments on nickel-oxygen systems have been performed throughout the years. As low primary energy EELS is very surface sensitive, the sample surface quality during the loss experiments is critical. Spectra taken on surfaces prepared by different techniques, do show deviations from each other. Especially the surface optical phonon energy and the appearance of inner gap surface excitons are very critical. Results obtained from for instance deposited films, oxygenated nickel crystals, sputtered surfaces, scraped surfaces, vacuum annealed surfaces and ex-situ cleaved crystals should in this context be critically considered. The preparation method dependent differences between the surfaces are an interesting point of surface scientific study in itself.

Reflection EELS results on ionic insulators like NiO can generally be separated into the following fields of interest, as is shown in Fig. IV.1: the vibrational spectrum ($0.1 < E_{\text{Loss}} < 0.4$ eV) represented in a magnified view, the inner-gap $d$-$d$ excitonic excitation spectrum ($E_{\text{Loss}} \leq E_{\text{gap}}$) and the study of high energy excitations across and/or far above the conduction gap limited by the mentioned charge transfer excitations ($E_{\text{Loss}} \geq E_{\text{gap}}$). The loss processes with large excitation energies will be partially discussed in the following wide scan section IV.C, the inner-gap excitons in section IV.D and the surface optical phonons in section IV.H.

IV.B Experimental Details

The energy loss measurements were carried out using a Vacuum Generators ARUPS10 angle-resolved electron spectroscopy system as discussed in detail in Chapter I. The hemispherical analyser, installed on a two-axis goniometer has been used in a $2^\circ$ aperture angle configuration during the experiments presented in this Chapter. Free rotation of sample and analyser enables us to select nearly any scattering geometry. The hemispherical electron monochromator unit is fixed to the mu-metal analysis chamber.

On another facility, small spot X-ray Photoelectron Spectroscopy experiments
have been performed to check the purity of the crystal, plus the stability of the \textit{in-situ} cleaved surface. Laue diffraction and Low Energy Electron Diffraction (LEED) have been used to check the crystal axes alignment. Azimuthal orientation of the samples will be indicated throughout this Chapter with respect to the reciprocal lattice vectors of the surface Brillouin zone\cite{10}. In this notation the [1, 1] direction in reciprocal space is parallel to the [1, 0, 0] direction in real space. Samples are cleaved in the preparation chamber after which they are transported to the analysis/main chamber. Basepressures at cleaving, before and during the measurements were $1 \times 10^{-10}$ mbar or better. Optimization of the EMU electron optics has been performed prior to cleaving. As a result EELS experiments could be performed within a few minutes after cleavage.

In the beginning of this project experiments have been performed on NiO crystals grown by the use of an elliptical mirror furnace\cite{8}. All of the results presented in this work have however been taken on NiO single crystals obtained from commercial supply\cite{9}. The appearance of the constant kinetic energy features, which has been proposed to arise from a fundamental process, has been found in both crystals.
IV.C Constant Kinetic Energy Lines in Wide Scan EELS

Wide scan energy loss results on NiO surfaces taken at medium or high primary energies have been studied by a number of groups [11, 12, 13]. Electronic excitations across the conduction gap and the appearance of the plasmon contributions originating from both bulk and surface have been studied as a function of primary energy, most often angular integrated. In this section we will concentrate on features which were not recognized at that time. In the previous Chapter the NiO(100) surface has been introduced as one of the insulating systems displaying pre-emergent effects in low energy electron scattering, resulting in constant kinetic energy features. The primary energy dependent spectra taken along the high symmetry directions show peaks above momentum dependent Bragg beam emergence conditions. Features with strongly changing intensity when crossing elementary excitation thresholds, appear at a number of characteristic kinetic energies. In this section the constant lines will be studied in more detail. Special interest will be given to remarkable structure as has been found along the [1,1] high symmetry line.

The wide scan specular EELS results along the [1,1]-direction have already been shown in Fig. III.20 as a function of kinetic energy. In Fig. IV.2 the same results are presented in the for EELS “standard” way; as a function of energy loss. First of all the very intense zero-loss peak can be recognized of which only the onset has been plotted. As the energy resolution is reduced so as to achieve a higher countrate at large energy loss regions, this peak is a combination of a symmetric real elastically scattered electron contribution and at the loss side the electrons that have suffered from vibronational excitations. In the region up to 4 eV energy loss weak features can be observed corresponding to the optically forbidden inner-gap d-d excitons [14]. The excitonic inner-gap contributions will be discussed in section IV.D. At around 4 eV the charge transfer (CT) process limited conduction band starts. The energy gap value found is in agreement with the combined XPS/BIS results (4.3 eV) published by Sawatzky and Allen [15].

Neglecting bandstructure related dispersion effects the mentioned features all appear in first order at constant energy losses ($E_{\text{Loss}}$). Also excitations of the inter band (surface)plasmons do follow this behaviour, but at these low primary energies they have a very low cross section and as a result are hardly recognizable. Contrary to the constant energy loss excitations, there is structure that is strongly dependent on primary energy. The cut-off, corresponding to the nearly zero kinetic energy electrons, moves per definition directly with the primary energy in this energy loss representation. There are however more features which seem to follow this relation at non-zero kinetic energies ($E_k$). These peaks can easily be selected from Fig. III.20. Contrary to the energy loss representation (Fig. IV.2), in the kinetic energy representation (Fig. III.20) all features at a constant loss energy move linearly with the primary energy, as $E_k = E_p - E_{\text{Loss}}$. The structures directly related to the primary energy show up at selected kinetic energies, as is
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**Figure IV.2:** Primary energy dependent specular EELS results along the [1, 1] symmetry direction of the NiO(100) surface. The primary energies ($E_p$) are indicated for the individual spectra, which are scaled to the height of the lowest constant kinetic energy peak.
Figure IV.3: Close-up of the low primary energy spectra taken along [1, 1], shown as a function of kinetic energy.

indicated by the vertical bars in Fig. III.20. The thin diagonal lines drawn in Fig. IV.2 can be directly related to sections of the vertical lines in the kinetic energy plot.

Contrary to the 6.2 eV constant kinetic energy line the one near 10.3 eV strongly changes in relative intensity. In the primary energy region 12-20 eV at energy losses above the CT band a strongly changing asymmetric structure has been found, as is shown in detail in Fig. IV.3. After a minor peak, which is only visible in a limited primary energy window, a relatively steep and narrow dip precedes the 10.3 eV feature, which forms the main intensity line. The most left vertical line is drawn to illustrate the minor reduction in peak energy near CT band crossing conditions. In this case the main part of the line moves below the threshold, as a result it seems as if the feature shifts to lower energies. The other
line is drawn to emphasize the individual minima. It is the combination of a maximum and a minimum structure that is so typical for Fano resonance related effects.

Coherent interaction between a discrete state and a continuum state has been discussed by Fano\cite{16} to result in strongly asymmetric structures. Depending on the sign of a dimensionless line shape parameter a minimum preceding a maximum can occur and vice versa. This line shape parameter is (among others) determined by the interaction between the two states. In our case loss processes before and after diffraction involving the waveguide condition will result in discrete and continuum states, as the waveguide condition can only be injected at special conditions. It is from this idea in combination with the appearance of the asymmetric structure involving both maxima and minima, that influence of a Fano resonance is considered as a possible origin for the remarkable structure in Fig. IV.3. In Fig. IV.4 this is demonstrated for conditions comparable to Fig. IV.3. When the two states do not interact coherently, a minimum in the background resulting from the loss processes across the gap will appear. This is comparable to the minimum in the elastic scattering intensity at direct conditions. A dip in the inelastic electron distribution will appear at the special conditions where they can fulfill the diffraction into the waveguide. Although the eye of a scientist is oftenly caught by peaked structures, it is to our opinion the combination of peaks and dips that corresponds to waveguide related structure.
Theoretical predictions achieved by calculation of the pre-emergent conditions as discussed in section III.H show reasonable agreement with the experimental constant kinetic energies. Within the emergent LEED beam scenario the 6.2 eV feature is possibly related to the tangential matching of the total wavevector with the equivalent (-1,0) and (0,1) lattice vectors. The strongly varying line is possibly related to matching of the (-1,1) vector, which in this case is parallel to the in-plane component of the incoming electron wavevector. A possible explanation for the multiple extrema within the strongly varying structure is the correspondence to different \( n \)-labelled surface states related to the same emergent condition. In EELS/LEED work on Ni(110) surfaces Rebenstorff et al.[17] showed that structure up to a few eV below threshold could be assigned to structure corresponding to \( n = 1, 2 \) and 3 Rydberg states. In this case the main line could correspond to the \( n = 2 \) and the minor peaks to the \( n = 1 \) and 3 contributions. Detailed LEED based theoretical studies will be needed to shed light on this interesting observation.

In order to investigate whether the asymmetric structure is restricted to specular conditions and/or momentum directions along the [1,1] direction, an extensive scattering geometry dependent study has been performed. Three series of fixed primary energy spectra have been taken along the [1,1] direction, as shown in Fig. IV.5. The spectra have been taken at 18 eV primary energy and 1.8 eV (EMU) respectively 5 eV (analyser) pass energies. The center panel contains the spectra taken at specular conditions with incoming/outgoing angles varying from 35 to 65 degrees, as is indicated. The 45°/45° scattering condition is taken as a reference, this experimental condition can be found in all three panels. The left panel shows the incoming angle dependence at fixed outgoing angle(45°), while the right panel shows the outgoing angle dependence at fixed incoming angle(45°). Because of experimental limitations the minima of the varying angles are not the same in the outer two panels. The width of the onset of the zero-loss contribution is more or less constant over the series of specular spectra. This is of course not the case in the two outer panels. The influence of the foot of the zero-loss peak on the detection of the weak \( d-d \) excitons is studied and discussed in section IV.D.

The structure of interest above the conduction gap is obviously not restricted to specular conditions. The constant features with energy values near 6 and 10 eV at 45°/45° show up in nearly the complete set of spectra at off-specular conditions, with only modest changes in intensity. This is in correspondence to the suggestion put forward in Chapter III that the constant energy features arise from secondary electrons fulfilling the pre-emergent Bragg conditions. We refer to secondary electrons in this case as electrons that are not related (anymore) to the primary electrons, disregarding the question whether their kinetic energy is low or not. Because of the indirect character of the waveguide excitation source, emission or scattering in a limited direction of observation, like the specular direction, is unlikely.

Considering the dispersion of both constant lines as a function of scattering
Figure IV.5: Scattering geometry dependence of EELS on NiO(100) along [111] and [100]

The incoming angle dependence is shown in the left panel, the specular variation in the center panel, and the outgoing angle dependence is plotted with as-taken intensities. The incoming angle dependence is shown in the left panel, the specular variation in the center panel, and the outgoing angle dependence is plotted with as-taken intensities.
geometry some interesting aspects appear. Within the all specular series strong
dispersion is found for the 10 eV line, only minor dispersion for the 6 eV line. The
direction of both dispersions is the same, lowering of kinetic energy when moving
towards grazing conditions. If we return to the calculated Kikuchi pattern for
NiO as is given in Fig. III.19, we can see that the branches ((-1,1),(-1,0) and (0,1))
that are supposed to be related to the 6 and 10 eV lines, disperse to lower kinetic
energies at increasing scattering angles. The dispersion of the upper branch
is in the angular region of consideration larger than for the lower branch. In
correspondence to the experimental results both branches converge to the same
value of around 8.5 eV. The strong dispersion is also found in the outgoing angle
dependent result(right panel), this time limited to the grazing scattering angle
region. The dispersion of the 10 eV line near normal conditions is nearly zero or
even seems to fold slightly backwards.

As the intensities are as-taken it is found that the region forming the conduc-
tion gap strongly looses weight when moving away from specular conditions. This
is also the case in the incoming angle dependent off-specular study(left panel).
In this case the dispersion of the constant line is however much smaller than in
the other two panels. At first glance the absence of a dispersion upon varying the
incoming angle contradicts the observation of dispersion in the theoretical results
of energy versus incoming angle. The fact that there is hardly any dispersion
is a result of, and supports the idea that, secondary processes are the driving
force behind the constant lines. During the energy loss process the electrons lose
the correlation to the incoming angle. The theoretical results for the direct case
are corresponding to incoming electrons diffracted parallel to the surface. In the
indirect case the reverse situation is created. Electrons with a given energy are
running parallel to the surface, to what angles are they diffracted? This is de-
scribed by exactly the same relation, but this time the angle of importance is the
outgoing angle.

Although the absolute energies of some of the lower kinetic energy lines are
too small, as discussed in the previous Chapter, the resemblance between theory
and experiment is significant. The dispersion of the higher energy line being
much stronger than that of the lower line, the apparent convergence to the same
energy for increasing angles and the kinetic energy of most of the features are in
agreement with the Kikuchi pattern results. Remember that, as the loss energies
are not much smaller than the excitation energies, standard theories like the
dielectric theory[18] are not valid. This region within EELS, with \((E_{\text{Loss}}/E_p) \gg 0\), has hardly been studied, because of the lack of theoretical descriptions.

From the results of Fig. IV.5 it is clear that at least along the [1,1] direction
the intense and asymmetric structure is observable in a large region of the Brill-
louin zone. The dependence on the azimuthal orientation while remaining under
specular conditions \((45^\circ/45^\circ)\) at 18 eV primary energy has already been presented
in Fig. III.21. The upper line moves slightly to higher kinetic energies, while the
lower line moves to lower kinetic energies, in agreement with the azimuthal de-
pendence in the Kikuchi pattern. The intense and characteristic structure above the conduction gap persists to azimuthal angles almost halfway $[1,1]$ and $[1,0]$, it is not restricted to a special region of the Brillouin zone as can be the case in symmetry-related bandstructure effects.

The primary energy dependent results as obtained along the other high symmetry direction $[1,0]$, are shown in figure IV.6. Some differences and analogies with the $[1,1]$ series come up. First of all the constant kinetic energy features appear at different energies. The feature at 6 eV is shifted down to 5.4 eV, from the azimuthal scan it is clear that the structures arise from the same condition probed at different momenta. The structure at 10.5 eV shows no resonant effect over the primary energy region probed and it does not appear stronger than a step-like feature. New compared to the $[1,1]$ spectra is the appearance of two constant lines at around respectively 18 and 21 eV. These features show up in a limited region near the CT band, like the peak at 30.25 eV.

The observation of related constant kinetic energy features in other electron scattering and emission based techniques, like photoelectron spectroscopy, has been stressed. The indirect process appears independently of the way the electrons are created. The figure in which McKay and Henrich[19, 20] compare their photoemission at 21.2 eV photon energy and electron beam ($E_p = 100$ eV) induced secondary electron emission spectra is reproduced in Fig. IV.7. Note the absence of the feature in the 40.8 eV excited spectrum, as the two photoemission spectra are aligned in binding energies and not in kinetic energies. The binding energies, indicated as initial energy, are aligned to the first peak in the PES spectrum and not at the chemical potential. The EELS spectrum and the photoemission spectra are aligned at the analyser cut-off, as such the term initial energy has no meaning for this spectrum. A feature at around 10 eV binding energy in a 21.2 eV excited photoemission spectrum has a kinetic energy relative to the vacuum level of the order of (21.2 - 10 - Work Function correction) eV. As the correction term is close to 5 this results in an energy familiar from our results of 6 eV. Comparison of the lowest constant line in the EELS results presented in this work and the feature indicated by the arrow in Fig. IV.7, shows that the appearances are comparable. The remarkable feature in the NiO results of McKay and Henrich had till today not been explained[20], from the close resemblance the feature is proposed to originate from waveguide related behaviour.

IV.D Excitonic d-d Excitations

Early optical spectroscopy results on NiO[14] showed weak features inside the optically forbidden conduction gap region. The lowest energy loss peak near 0.24 eV has been related to spin conserved double spin-flip processes, called two magnon excitations[21]. In relation to the work presented here the features observed at slightly larger energy losses in the 0.5 - 4 eV range are of more interest. Weak features have been found which are related to excitonic states of the
Figure IV.6: Primary energy dependence of the specular EELS results along the [1,0] symmetry direction of NiO(100). Spectra are scaled to the intensity of the lowest energy constant feature.
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![Photo emission spectra](image)

**Figure IV.7:** Photoemission spectra drawn by straight lines and electron beam induced secondary electron emission spectrum drawn by the dashed line as taken on NiO(100) by McKay and Henrich (1984). The term initial energy corresponds to the binding energy for the included photoemission spectra only.

Ni\(^{2+}\)(3\(d^8\))O\(^{2-}\)(2\(p^6\)) groundstate of this ionic compound. The eight 3\(d\) electrons can be arranged over 10 Ni 3\(d\) spin resolved levels in any arbitrary combination, as long as the Pauli principle is satisfied. Important parameter in the energy levels of the d-d excitons is the symmetry dependent crystal field splitting. The Ni 3\(d\) orbitals in the bulk NiO \(O_h\) symmetry are split into \(e_g\) and \(t_{2g}\) orbitals. The first class consists of the \(d_{x^2-y^2}\) and \(d_{3z^2-r^2}\) orbitals. The second group contains the \(d_{xy}\), \(d_{xz}\), and \(d_{yz}\) orbitals. Rearrangement of the Ni 3\(d\) electrons over these levels relative to the energetically lowest 3\(d^8\) ground state combination, the two remaining holes spin parallel in the two \(e_g\) levels, results in localized excitonic states related to \((3d^8)^*\). The \((3d^8)^*\) combinations have a higher energy and exist only as excited states. Because of conservation of angular momentum (\(\Delta l = 0\)) the 3\(d^8\)-(3\(d^8\))^* excitation abbreviated to d-d excitation, is optically forbidden. The presence of optical phonons induced by the probing radiation, reduces the local inversion symmetry at the Ni ion. As a result of the displacement induced by the optical phonons \(p\) character will mix in and a certain sensitivity to optical spectroscopy will result.

As discussed in section I.D excitations that can be studied by the use of Electron Energy Loss Spectroscopy are not restricted to optically allowed processes. Especially at low primary energies EELS has been shown to be very useful in studying the origin of inner gap excitations\(^{[22, 13]}\) in transition metal oxides. The experimental results on d-d excitation energies can be compared to theoretical studies performed with a variety of models and techniques. Because of
the “limited” structure that needs to be calculated for localized $d$-$d$ excitonic excitations, resulting from the involved localized $3d$ electron orbitals, a variety of theoretical models can and has been used, among which: impurity model[23], cluster calculations[24, 25], atomic R-matrix theory[26], and quantum chemical calculations[27, 28, 29, 30].

Depending on the in or out-of-plane character of the $d$-levels involved, excitonic levels shift in energy when the Ni ion surrounding is altered from NiO$_6$ for the bulk to NiO$_5$ at the (100) surface. Corresponding to a reduction in symmetry from $O_h$ to $C_{4v}$. This is shown in the two upper panels of Fig. IV.8, where the $d$-$d$ exciton excitation energies for the $C_{4v}$[30] and $O_h$[29] symmetries as derived by quantum chemical models plus the corresponding exciton labels are given. Thin lines are drawn between corresponding excitons in both symmetries.

As low energy EELS is surface sensitive, symmetry reduction induced $d$-$d$ exciton levels can be probed as well as the bulk related contributions. Studying the inner gap structure as a function of primary energy and scattering geometry, can possibly distinguish surface from bulk originating excitons. A NiO$_5$ related $d$-$d$ exciton around 0.6 eV los energy has been reported in EELS studies by Freitag et al.[28] and Gorschlüter and Merz[13]. Based on quantum chemical calculations performed by Freitag et al.[28] this feature has been related to a $^3E$ surface exciton. This surface exciton can be easily recognized in the two lower panels of Fig. IV.8. The fact that this peak can only be observed on freshly cleaved surfaces supports the assignment to a NiO$_5$ related exciton. Experiments by Fromme et al. have shown that atomically clean single crystalline surfaces are required to observe the 0.6 eV feature[31]. From the shape of the peak as it appears in the two lower panels of Fig. IV.8 a double structure assignment resulting from excitations at 0.55 and 0.65 eV is possible, especially when the features are related to the “narrow” 0.55 eV structure in the 29.5 eV excited spectrum.

Other excitons are found at at least 1.05 eV (especially in the 18 eV spectrum), 1.25 eV, 1.5 eV, 1.68 eV, 1.85 (weak), 2.15, 2.7, 2.8, 3.2, and 3.45 eV. The high intensity of the excitonic line at 2.15 eV under grazing conditions points in the direction of a surface related origin as has been proposed by Fromme and co-workers, who studied the polarization dependence of the excitonic excitations[32]. This line has by far not been observed before as intense as in Fig. IV.8. Despite the large interest from theoretical studies in the NiO exciton excitation energies, hardly any experiments have been performed with a resolution in combination with an angular independence of incoming and outgoing angles, which now seems to be required to resolve the variety of surface and bulk exciton energies. Comparable exciton studies have been performed on CoO(100), both theoretical[33] and experimental[34] ones.
Off and near specular results on the d-d excitons in the conduction gap region of NiO(100). The experimental conditions of each of the spectra are indicated inside the panels, all spectra were taken parallel to the [1,1] direction. In the two upper panels the quantum chemical theoretical d-d exciton excitation energies under $O_h$ and $C_{4v}$ symmetries are reproduced from de Graaf and Geleijns respectively.
IV.E  Masking of the $d$-$d$ Excitons by the Elastic Contribution at Specular Conditions

Optically forbidden $d$-$d$ exciton studies are most often, like other EELS studies, performed under specular conditions. The relative cross section of the $d$-$d$ excitons with respect to the cross section of the surface optical phonons is of the order of 0.001 or less. As the $d$-$d$ excitonic contributions are so weak, care should be taken especially at the mentioned specular conditions. Figure IV.9 shows the outgoing angle dependent results on the conduction gap region, taken at 18 eV primary energy along the $[1,1]$ high symmetry direction. Along this symmetry direction and near this primary energy no influences are expected from waveguide conditions inside the conduction gap region. As the beam current was only of the order of $5 \times 10^{-11}$ A, charging effects did not appear and serious radiation induced damage was prevented. In the top panel the as-taken zero-loss intensity of each of the spectra included in the lower panel, is shown to be strongly peaked around specular conditions. The width of the elastic intensity maximum is of the order of the used analyser acceptance angle (2$^\circ$). The onsets of the individual zero-loss peaks can be recognized in the two absolute intensity panels below. The left panel shows the angular dependence from grazing scattering towards specular conditions, the right panel from normal scattering towards specular.

In the spectra labelled by the outgoing angle a number of contributions can be recognized. The combined elastic scattering and optical surface phonon contributions near zero loss energies strongly increase in weight near specular conditions. At maximum the onset extends to at least 0.5 eV energy loss. Near specular conditions a minor peak is found at 0.55 eV energy gain which is related a hardware defect and does not belong nor contribute to the physical energy loss or gain processes. Away from specular conditions the surface exciton at 0.55 eV energy loss can be recognized. It is obvious from the spectral series that a maximum intensity region exists at 1.5 - 2$^\circ$ off specular toward the surface normal side. Other much weaker excitonic contributions are found at 1.05, 1.7, 2.15, 2.8 and 3.2 eV loss energy, as has been in the previous section. None of the exciton lines show a detectable dispersion in the momentum region probed. The maximum momentum transfer for the zero-loss energy in this series if 0.3 Å$^{-1}$ for the spectrum at 35$^\circ$ incoming angle. This is in correspondence to the localized character of the $d$-$d$ excitons. Contradictory to the preference of performing loss experiments at specular conditions, it becomes clear from Fig. IV.9 that the specular conditions are the less favourable conditions to study the excitonic lines.

This is even more pronounced when we plot the same series of spectra in a three dimensional representation, as is shown in Fig. IV.10. The minimum intensity inside the conduction gap region is lifted by the large energy loss onset of the zero-loss peak. As a result of the strong zero-loss contribution the weak excitonic structure is overshadowed. Based on this series the optimal conditions to measure the excitonic structure is proposed to be on the normal side of the
Figure IV.9: Emission angle dependent d-d exciton spectra on NiO along [1, 1] at 45° incoming angle and 18 eV primary energy. The upper panel contains the elastic scattering intensity as a function of outgoing angle. The indicated angles are relative to the surface normal.

specular conditions just out of the dipole lobe, as has been used in two of the spectra in Fig. IV.8. Performing experiments at these near-specular conditions circumvents analytical zero-loss subtraction procedures to resolve weak excitonic contributions. The influence of the specular beam onset on the observation of weak features is especially severe when the analyser acceptance angle is of the
order or smaller than the dipole lobe, as is the case here. Reported energy loss experiments are most often performed with larger acceptance angles or even angle integrated. In these situations the spectra of Fig. IV.9 should be integrated. As such the excitons will appear as being much stronger while they contribute in nearly all the spectra. The zero-loss line only contributes in a narrow lobe which spans only a small part of the analyser acceptance angle.

Initiated by technical developments energy loss experiments on optically forbidden excitations are more and more performed under narrow acceptance angle conditions. In these studies the discussed phenomenon should be critically considered. Of course the surface flatness plays a role too. Improvements in crystal
growth techniques have resulted in more systems from which \textit{in-situ} cleaved surfaces can be studied. Nicely cleaved surfaces result in intense and narrow dipole lobes, increasing the dominant influence at specular conditions.

\textbf{IV.F \ Intensity Enhancement of $d$-$d$ Excitons at Waveguide Conditions}

Surface Electron Waveguide behaviour as discussed in this thesis has been shown to result in extrema of the elastic scattering intensity and in the occurrence of features with momentum dependent constant kinetic energies. Excitation energy dependent intensity studies on elementary excitations are usually performed under normalization to the zero-loss line intensity which is assumed to be constant. Based on the mentioned observations it is reasonable to expect the most often neglected fundamental waveguide process to have multiple effects on such primary energy dependent studies. Direct scattering processes cause fluctuations in the zero-loss line intensity, as is shown in numerous LEED studies\cite{35}. Because of the normalization to the height of the zero-loss line primary energy dependent variation in the inelastic/elastic scattering intensity ratio is expected. The influence of indirect waveguide processes is less straightforward. It has been shown in the wide scan results that waveguide related features appear when the cross section of the loss process, required to reduce the electron energy to the matching conditions, is unequal to zero. Although the exciton cross section is small, the excitation of the $d$-$d$ excitons can be used by the incoming electrons to end up in the waveguide condition. Especially as there are no other possibly more intense, excitations available in this energy range, because of the conduction gap.

In Fig. IV.11 the primary energy dependence of conduction gap region is shown, obtained along the [1, 0] directions at scattering angle conditions equal to 45°/45° and normalized to the height of the zero-loss line. The full width spectra have been shown in Fig. IV.6. In the wide scan spectra the constant lines are indicated by straight diagonal lines. From the spectra in Fig. IV.11 the intensity of the 1.7 eV exciton has been derived, corrected for the background intensity. These intensities are plotted in the right panel as a function of primary energy. Strong enhancement is found at primary energies near 15, 20, 22 and 32 eV. In the top part of this panel the kinetic energies of the constant lines as obtained from Fig. IV.6, increased by the energy loss of the exciton (1.7 eV) have been indicated by arrows. In this way the primary energies at which the constant lines cross the 1.7 eV exciton are marked. Strong resemblance is observed for the three upper lines. The lowest resonant primary energy does not match with the lower constant energy line arrow. At these low primary energies, where the loss/elastic energy ratio is (1.7/15 = 0.113) much larger than zero, strong interactions of a different character can arise.

In EELS studies on NiO by Gorschützer and Merz\cite{13, 36} and by Fromme and co-workers\cite{37} strong exciton intensity resonances and polarization dips in spin-
Figure IV.11: Exciton intensity enhancement at constant line crossing conditions. The panels on the left display the inner gap regions at specular conditions from $E_p = 12$ (bottom) up to 25 eV(top) and from 26(bottom) to 41 eV(top). The right panel shows the intensity of the 1.7 eV exciton as a function of primary energy.

resolved experiments have been reported at primary energies of 30, 38 and 102 eV. These experiments have been performed under $45^\circ/45^\circ$ scattering conditions, the azimuthal orientations have not been indicated. The lowest resonance primary energy reported is in close agreement (30 eV) to one of the constant kinetic energy feature zero-loss line crossings reported in this work. As has been shown in Fig. IV.11 exciton enhancement has been observed in this primary energy range. The lower resonant primary energies have not been probed in the experiments quoted. The 30 eV resonance in the work of Fromme et al.[37] has been related to O2s $\rightarrow$ Ni4s transitions. This Auger process would result in a remaining excited 3$d^8$ electron state and as such explain the resonant effect. It is at this moment not possible to exclude the influence of Auger processes in the 30 eV resonance. From Fig. IV.6 is clear that the line at 30 eV kinetic energy is not observed inside the conduction gap. In the case of electron emission resulting from Auger processes no such restrictions to the appearance of the emitted electrons are expected.
IV. The use of the Waveguide Principle in the Study of Elem. Excitations

IV.G Temporary Negative Ion Resonances

Strong electron scattering resonances, most often in phonon excitation studies, are observed as a function of incoming energy, resulting in enhanced intensity of loss features and reduction of angular correlation\cite{38}. Trapping of electrons based on the effect that incoming electrons directly occupy states in the unoccupied DOS is a known phenomenon in electron scattering studies on adsorbate systems. Contrary to normal energy loss features, where it is the convolution of occupied and unoccupied density of states that results in peaks, as in Fig. III.5, the incoming electrons directly occupy unoccupied levels. Variation of incoming and/or outgoing angle results in strong variation of the intensity of the process, in relation to the orientation of the “to be occupied” electron wavefunction lobes. This process that is known as Temporary Negative Ion (TNI) resonance, has also been reported to be observed in high resolution EELS on NiO(100) surfaces\cite{39}. If correct this would be one of the first observations of TNI resonances on clean and well-defined crystalline surface.

The TNI resonant primary energies relative to the vacuum level can be estimated from Bremsstrahlung Isochromat Spectroscopy (BIS) results, another expression for Inverse Photoemission Spectroscopy (IPES) at high electron energies. Figure IV.12 shows an artist’s impression of the BIS spectrum of NiO(100)\cite{15, 36} as is obtained with 1487 eV electrons. The energy difference between vacuum level and the individual peaks corresponds to the resonance energies. As the primary electrons are trapped inside the solid, the energies in vacuum and solid have to be matched. An offset energy value in the range of the inner potential or work function (3-10 eV) should be considered. Under the assumption that $E_F$ is pinned, which is not trivial in the case of insulators, and that the work function

![Graphical impression of the TNI resonance energies of NiO(100) in relation to peaks in the inverse photoemission spectrum.](image)

\textbf{Figure IV.12:} Graphical impression of the TNI resonance energies of NiO(100) in relation to peaks in the inverse photoemission spectrum.
IV.G. Temporary Negative Ion Resonances

**Figure IV.13:** Logarithmic representation of the primary energy dependence of the first phonon to elastic scattering ratio as taken from Wulser and Langell, *Phys. Rev. B* **48**, 9006 (1993).

is equal to 4.4 eV[20], we can derive from Fig. IV.12 that 5.0 (3d⁶ → 3d⁸ 4s¹), 8.5 (3d⁶ → 3d⁸ 4p¹) and 13.5 eV (3d⁶ → 3d¹⁰ L) can correspond to TNI resonant energies. The strongest TNI resonance ((3d⁶ → 3d⁸) as the 3d⁶ line is more intense than the other BIS peaks) can not be probed by EELS, as this would require negative kinetic energy electrons. An example of a material in which the lowest BIS state can be probed by EELS is Eu metal, as can be derived from the combined XPS/BIS results on the rare earths[40], which have been theoretically studied by Van der Marel and Sawatzky[41]. Lowering of the work function by the use of deposition processes is another way to make TNI resonances achievable from the most intense BIS state.

EELS experiments on NiO studying possible TNI influences on the relative intensities of the surface optical phonons have been reported. Figure IV.13 shows the reproduced phonon intensity data from Wulser and Langell[39]. From the vibrational energy loss spectra taken on argon-ion sputtered and vacuum annealed NiO surfaces, the relative first phonon–zero-loss intensity ratios have been extracted by the use of peak fitting techniques taking into account severe asymmetric line shapes caused by so-called tailing effects. Relative phonon enhancement is found at energies comparable to the TNI resonant energies listed before. The predicted theoretical dependence as indicated by a straight line will be discussed below, together with the primary energy dependent optical phonon spectra taken on in-situ cleaved NiO(100) surfaces in relation to possible TNI resonances.
The energy of the incoming electrons during energy loss studies is however much smaller than the 1487 eV energy scale probed in the quoted BIS experiments. It is questionable to assume that the unoccupied density of states probed by electrons in the low energy regime is the same. The 1487 eV excited BIS spectrum is quite different when compared to the 9.7 eV excited IPES spectrum[42]. Whereas the features are well resolved in the high energy case, a rather structure less spectrum is found at low primary energies. The absence of maxima in the IPES spectrum at an energy scale equivalent to the EELS electrons contradicts the observation of distinct TNI related resonances.

IV. H Fuchs-Kliewer Phonon Intensity Study

In this section we will study the absolute and relative intensities of the surface optical phonons as a fingerprint of resonant electron scattering processes. Some resonant effects can result in an increased time spent by the electrons in the vicinity of the surface, relative to non-resonant electron scattering conditions. Consequently the probability to lose energy by excitation of loss processes, among which phonons, will increase. The phonon structure itself will however not be studied in detail in this work, although some basic theoretical relations will be discussed. In papers on the lattice dynamics of NiO by the use inelastic neutron scattering[43], and the surface phonon dispersion on rock-salt structure compounds studied with EELS[44], detailed phonon studies are presented. Next to studies on the NiO(100) surface system, a large number of vibrational energy loss studies on oxygenated nickel surfaces have been performed[45, 46, 47] initiated by the interest in catalytic surfaces. Reviews on the achievements in understanding the vibrational properties of oxide surfaces can be found in the book by Henrich and Cox[20] and in two successive papers on oxide surfaces by Freund et al.[48] in which also EELS studies on absorbate systems on NiO(100) surfaces are discussed.

Vibrational spectra of NiO(100) studied with low energy specular EELS are dominated by the appearance of the surface optical phonon and its higher order contributions, like in most of the ionic insulator studies including the previously discussed Sr$_2$CuO$_2$Cl$_2$ results. The dipole field induced by the relative displacement of opposite charges extends far into both vacuum and sample. As a result low energetic incoming electrons couple strongly to this field. The related phonon structure is much stronger than contributions from other lattice vibrational modes. Solving the Maxwell equations and applying the boundary conditions at the surface shows that these so-called Fuchs-Kliewer[6] mode phonons arise at the condition[18, 49, 20, 50] that the real part of the frequency dependent dielectric constant($\varepsilon(\omega_{FK})$) equals -1. Theoretical values[45] for the Fuchs-Kliewer surface phonon energy $\omega_{FK}$ for NiO are calculated from the relation,

$$\omega_{FK} = \left(\frac{\varepsilon_0 + 1}{\varepsilon_\infty + 1}\right)^{1/2} \omega_{TO}$$

(IV.1)
with $\varepsilon_0$ (11.75) and $\varepsilon_{\infty}$ (5.7), respectively as the static and high frequency dielectric constants and $\omega_{\text{TO}}$ the transverse optical phonon energy. Solving this relation while taking care of the uncertainties in the parameters, gives that the Fuchs-Kliewer phonon energy for NiO is expected to lie between 67.9 and 69.3 meV.

Considering the intensity ratios as they appear in vibrational energy loss spectra the following relations have been derived. From the classical loss probability as determined in the dielectric theory it has been derived that in the case of intrinsic surface phonons, under the condition that the ratio $E_{\text{Loss}}/E_p$ is small, the phonon versus elastic intensity is given by:

$$I_{\text{ph}}/I_{\text{elastic}} \simeq (\cos \theta)^{-1} E_p^{-1/2} \omega_{\text{FK}}^{-2}$$

(IV.2)

with $I_{\text{ph}}$ as the first phonon intensity, $I_{\text{elastic}}$ the intensity of the zero-loss peak and $\theta$ as the outgoing angle. At fixed conditions of both $\theta$ and $\omega_{\text{FK}}$ a $E_p^{-1/2}$ dependence of the relative intensity ratio between first phonon and zero-loss line is found. For adsorbate related lattice vibrations different dependences on primary and phonon energy are found.

The strength of the coupling between incoming electrons and Fuchs-Kliewer phonons at low primary energies results in significant contributions from higher order phonon losses. Under the assumption of single harmonic behaviour, as is the case in the isotropic NiO system, the intensity distribution of multiple losses can be described by Poisson statistics[18]. Experimental electron momentum dependent deviations from the theoretical intensity relations can arise from resonant effects. The restriction to conditions with small $E_{\text{Loss}}/E_p$ ratios originates from the limitations of dielectric theory. As discussed in section I.D the angle in between the specular direction and the first phonon dipole lobe is directly related to the $E_{\text{Loss}}/E_p$ ratio, and moves into the direction of the surface normal for increasing $E_{\text{Loss}}$-values. At conditions where the dipole lobe becomes of the same order as the analyser acceptance angle the phonon/elastic intensity ratio is influenced by hardware related effects. The restriction to small $E_{\text{Loss}}/E_p$ ratios and the $2^\circ$ aperture angle used during the experiments, prevents hardware influences even in the case of the multiple phonon lines in the phonon results discussed here.

As discussed in the preceding section electron confinement in TNI resonances has been proposed[39] to result in enhancement of relative phonon intensities. In Fig. IV.13 deviations from the primary energy dependence as introduced in equation IV.2 are assigned to conditions at which incoming electrons can directly occupy unoccupied states. The surfaces have been prepared by cycles of Argon-ion sputtering and vacuum annealing. Tailing functions had to be introduced during the fitting procedure to subtract background effects. Whereas the asymmetry is claimed by the authors to be representative for semiconducting surfaces, it is our opinion that it is possibly related to the surface preparation. This is supported by the data presented in the discussion[51] of the integrity of the used surfaces as a function of Ar$^+$ sputtering. Vibrational loss experiments on well prepared
comparable monoxide surfaces[18, 49] contain symmetric lines that can be fitted by a combination of Lorentzian and Gaussian peaks only. Enthusiast about the resonant process itself, but anxious about their assignment of measurements on a NiO(100) representative surface, we performed primary energy dependent energy loss series of phonon spectra on in-situ cleaved NiO.

Vibrational specular spectra have been taken as a function of primary energy along the two high symmetry directions. Under the assumption of Poisson distributed phonon intensities and taking \( j \) as the phonon order, the dataset \( \ln \left( \frac{(I_j \times j!)}{\left(\sum_{i=0}^{j} I_i\right)} \right) \) versus \( j \) will result in a straight line. From equation IV.2 it is clear that the slope of this line should be proportional to \( E_p^{-1/2} \). Figure IV.14 shows the results obtained along the high symmetry directions of NiO(100). From the spectra shown in the left panel, taken along the [1, 0] direction the phonon quantum energy is found to be 68 (± 0.5) meV, in close agreement to the theoretical prediction discussed above. The structures in the spectra are nicely symmetric and the minima in between the narrow peaks are close to zero intensity. In the panels on the right in Fig. IV.14 the fitted Poisson slopes of the spectra for both the [1, 0] and [1, 1] direction are plotted versus \( \ln E_p \). The error bars indicate the error resulting from the fit through the Poisson distribution. The error occurring in the determination of the individual intensities has not been included. In this excitation energy range the intensity of at least up to the third \((j=3)\) phonon contribution has been fitted. This is substantially more accurate than the plots published by Wulser. In their case only the first-phonon/zero-loss ratio is taken after performance of a tailing correction.

From the panels on the right in Fig. IV.14 in comparison to Fig. IV.13 it is clear that we have not been able to reproduce the phonon enhancement at the TNI energies. Phonon enhancement near primary energies of 5.5-6 eV have been observed along [1, 0] and near 10 eV along [1, 1]. The arrows drawn in the panels correspond to the lowest emergent energies for each of the high symmetry directions as derived in section III.H. Although the primary energy range probed along [1, 0] is too narrow to draw conclusions, the results along [1, 1] clearly show phonon enhancement at primary energies near the emergent condition. Also along [1, 0] a maximum is found corresponding to the emergent energy. Based on the correspondence to the observed kinetic energies of the constant features induced by waveguide related effects, the proven phonon enhancement in metallic waveguide studies, see section III.B.1 and the results on the vibrational spectra of Sr₂CuO₂Cl₂ in the previous Chapter, pre-emergent Bragg diffraction induced waveguide effects on NiO(100) are proposed to result in the phonon enhancement at 6 and 10 eV.

Phonon enhancement as a result of emergent Bragg diffraction conditions can be studied at low primary energies, corresponding to tangential matching with the shortest lattice vectors, as was the case above. In the wide scan results we have shown that also in the primary energy region near 30 eV constant kinetic energy lines have been observed. It is near this energy that Cox and Williams[52] have
Figure IV.14: Primary energy dependence of the optical surface phonons along the [1,0] and [1,1] directions. The left panel contains the spectra taken along the [1,0] direction normalized to the height of the zero-loss peak. The right panels contain the analysis of the fitted slopes of the Poisson distribution of each spectrum as a function of primary energy. The arrows indicate the lowest energy emergent conditions as result from theory.

reported possible phonon enhancement in experiments on MgO. Up to the 12th-order phonon can be recognized in a spectrum taken at 30 eV under specular conditions. Normally the highest order phonon that can be recognized in this excitation energy range is 4! Although Cox and Williams were at that time not able to reliably reproduce the extended phonon structure, they discussed in an appendix the possible origin of diffraction into a surface state. In the as forthcoming quoted publication, finally published as [53], the idea has been
Figure IV.15: Phonon spectra taken at primary energies in the vicinity of the \((-2,1),(-1,2)\) beam emergent condition.

developed into a description of surface excitons on ionic crystals. Recent work\[54\] has shown that this description is not correct.

Figure IV.15 contains two spectra taken along the \([1,1]\) direction of NiO. Whereas the multiple phonons in the “standard” 30.6 eV spectrum can be distinguished up to the 3\(^{rd}\) order, up to the 8\(^{th}\) order contributions can be recognized in the 31.6 eV excited spectrum. The vibrational energy quanta remain constant up to the highest mode: a situation comparable to the 30 eV excited MgO spectrum of Cox and Williams. It must be noted that the first phonon/zero-loss ratio in the case of the MgO spectrum (~ 0.41) is much larger than our value 0.23. As the lattice parameters of both monoxides are comparable \(a(\text{MgO}) = 4.211\) Å relative to \(a(\text{NiO}) = 4.168\) Å\[20\], the emergent Bragg beam conditions will be nearly the same with slightly smaller energies for MgO, 31.6 respectively 32.2 eV for the (-1,2) branch.

The spectra depicted in Fig. IV.15 are taken from a primary energy dependent series. The absolute first phonon and the relative multiple phonon intensities are derived from each spectrum and plotted as a function of primary energy in Fig. IV.16. Strong enhancement of the as-taken first phonon intensity is found in the upper panel near a primary energy comparable to the kinetic energy of the constant line in the wide scan series (29.2 eV), indicated with an arrow. The same behaviour is found for the elastic scattering and the higher order phonon contributions. The intensity in the elastic contribution even becomes so intense that channeltron saturation effects are expected to influence the relative phonon/zero-loss intensity ratio. For that reason we have considered the first phonon intensity.
Figure IV.16: Primary energy dependence of the absolute first phonon intensity (upper panel) and relative intensities of the odd higher order phonons (lower panel) near the \((-2,1),(-1,2)\) beam threshold condition along \([1,1]\).

Significant relative enhancement of the higher order phonon excitations is observed in an energy window around 31.5 eV. The weights of the higher order phonons are normalized to the intensity of the foot of the elastic peak at the multiple phonon energy region. This corresponds to normalization to the elastic scattering intensity, as the shape of the zero-loss line and thus the ratio between peak height on onset remains constant. Enhancement of the relative phonon intensities for increasing primary energies automatically results in deviation from Poisson statistics and thus from description by the dielectric theory. Electron confinement is a known cause of multiple phonon enhancement fingerprints. Figure IV.16 clearly shows that the wide primary energy region of absolute enhancement is separated from the narrow energy window of relatively stronger multiple
phonons. Beam threshold calculations performed in the previous Chapter resulted in a theoretical value of 32.2 eV for the conditions under consideration. As 31.5 eV is still well below this value, it is possible that both the absolute enhancement and the relative enhancement of multiple contributions originate from resonant phenomena related to the same Bragg diffraction condition, but corresponding to different \( n \)-indexed surface states. As has already been shown in Fig. IV.11 \( d-d \) exciton enhancement has been observed in the same primary energy range 30-32 eV along the same symmetry direction and identical scattering angles.

IV.1 Conclusions

Constant kinetic energy features in the energy loss spectra on \textit{in-situ} cleaved single crystalline NiO(100) have been studied at specular and off-specular conditions. Minor influence of the incoming angle and strong influence of the outgoing angle, resulting from the inelastic character of the waveguide injection, has been observed. Convergence of different constant lines when considering grazing scattering conditions has been found in agreement with theoretical emergent conditions, as well as different dispersion directions of the constant lines as a function of azimuthal orientation. Strong interference effects between loss process features across the Charge Transfer gap and waveguide related features are observed.

Resonant effects have been found for direct scattering near 30 eV primary energy. Enhancement of the absolute elastic and phonon contributions are found at the conditions where the constant line crosses the zero-loss kinetic energy. Phonon enhancement up to the 8\textsuperscript{th} order, in this way clearly diverging from dielectric theory, has been found in a narrow primary energy region just above, but well separated, from this absolute intensity resonance. Nevertheless the phonon resonant condition is still below the theoretical corresponding emergent energy. We have not been able to reproduce Temporary Negative Ion resonance related structure in the primary energy dependent phonon loss distribution on NiO(100)[39]. Phonon enhancement has been observed however at primary energies in correspondence to the theoretical lowest energy emergent conditions.

Exciton intensities in a zero-loss intensity normalized representation have been proven to increase at primary energies equal to the constant line plus the considered \( d-d \) exciton loss energy. The resonances are not found at primary energies equal to the constant line energies, which would indicate relative enhancement from elastic scattering reduction only. Exciton enhancement follows when a constant line crosses the exciton energy in the primary energy dependent energy loss representation, as a result interference effects between constant lines and excitonic excitations are probable.

From extensive primary energy dependent studies we have shown that the momentum dependent waveguide conditions can be used to enhance the intensity of the loss process of interest. The influence of the interference effect on the intensity of surface optical phonons and inner gap \( d-d \) excitons has been demonstrated.
Bibliography


