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LETTER TO THE EDITOR

Anomalous electron energy-loss spectra of Ni(430) and a disordering of atomic steps

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Abstract. We present energy-loss spectra (ELS) in the range 0–20 eV taken as a function of temperature (90–800 K) and primary energy (100–400 eV) for a Ni(430), or $[\frac{7}{2}(110) \times \frac{1}{2}(100)]$, surface. A strong primary-energy dependence of ELS and pronounced differences within the ELS of the low-energy electron diffraction beams were observed. These characteristics arise from the presence of ordered atomic steps on the surface, as shown by a model calculation. We also observed temperature-dependent variations of the ELS, and interpreted them as being induced by a structural transition of the surface.

Clean stepped nickel and copper surfaces [1] have been observed to undergo structural phase transitions which are interpreted as roughening transitions [2]. These studies, using helium-atom diffraction, have been carried out for $(11n)$ surfaces having (001) terraces separated by monatomic steps. In the present study a (430), or $[\frac{7}{2}(110) \times \frac{1}{2}(100)]$ [3], surface has been chosen, where (110) teraces are separated by monatomic steps as shown in figure 1. At lower temperatures we have found novel features in electron energy-loss spectral (ELS) which can be explained by the diffraction of the plasma wave by the ordered steps. A proper understanding of the spectra is important for the study of electron excitation at the surface (e.g. the screening of a charge carrier). At $T > 400$ K the ELS vary until they resemble those of a flat (110) surface, indicating a structural phase transition of the surface. This could be an order–disorder transition in the step structure, possibly similar to a roughening transition such as is observed for the Ni and Cu $(11n)$ surfaces.

The UHV chamber was equipped with a retarding-field analyser for Auger electron spectroscopy and ELS. A video LEED system and a spot photometer were used to measure the elastic and inelastic LEED intensities as a function of primary energy and temperature. The base pressure during the measurements was 4×10^{-9} Pa. The Ni(430) sample had the shape of a disc, 1.5 mm thick and 8 mm in diameter. The orientation of the (430) surface is 8.1° off the (110) plane in the $[1\bar{1}0]$ direction (figure 1). The orientation of the crystal lattice was checked by x-ray diffraction with a precision better than 0.5°. To

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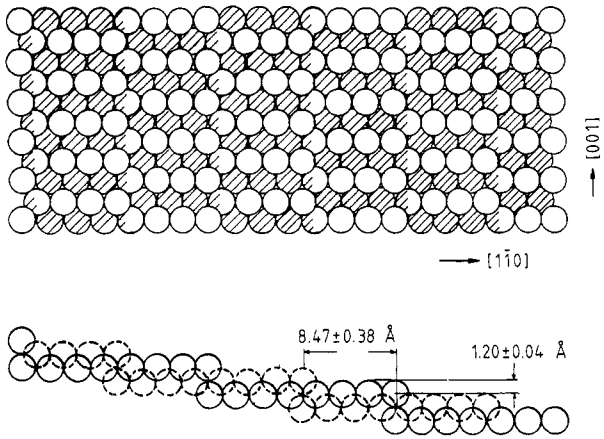

Figure 1. Top and side views of a hard-sphere model of the Ni(430) surface. The hatched atoms are partly covered by the step-edge atoms.

remove surface contamination, mainly by carbon and sulphur, two cleaning procedures were used, namely initial sputtering and annealing at 1100 K [4] and final chemical treatment using O_2 and H_2 [5]. The cleanliness of the surface and the bulk ultimately attained was such that even after the sample was kept for 4 h at 1000 K a sulphur coverage of less than 1% was detected. A sharp LEED pattern representative of a (430) surface having well ordered steps was observed below 260 K after these treatments. We have confirmed the geometry of the surface shown in figure 1 by a kinematic LEED analysis, following Henzler [6]. The LEED spots are indexed in the present paper according to the (110) LEED pattern, allowing for the splitting of the out-of-phase spots [6] due to the presence of steps. The ELS measurements were performed at normal incidence (±2°) of the electron beam with respect to the (110) terraces.

The total range of the primary energy for ELS was $100 < E_p < 400$ eV. An example of a set of integral ELS, taken by collecting the total current on the LEED screen, is shown in figure 2. The sample temperature was kept at about 90 K. The loss spectra reveal a strong dependence on E_p. In figure 3, where the primary-energy steps ΔE_p are only 0.2 eV, it is shown that the details of ELS vary, from spectrum to spectrum, with small primary-energy increments. It is to be noted that in the primary-energy range of figure 3 the number of LEED spots on the screen remains constant.

As far as we know, this kind of rapid change of electron energy-loss features with E_p is being reported here for the first time. The spectra obviously show a LEED effect (cf e.g. [7]). For studying the LEED effect more closely, spot photometer measurements were carried out at different LEED spots, as shown in figure 4. It was found that a significant contribution to the ELS could be recorded only at a LEED spot and in its close vicinity, indicating that the integral ELS shown in figures 2 and 3 contain primarily the contributions of the LEED spots. In figure 4 the symmetrical pair of LEED spots (1, −2) and (1, 2) have, within experimental error, an identical spectrum. All the other measured spots have different symmetries, and accordingly different spectra. It has been found generally that the structure of the spectrum is equally anomalous (E_p-sensitive, complicated profile) for the out-of-phase (split) and in-phase (unsplit) beams in the LEED pattern (for terminology see [6]).

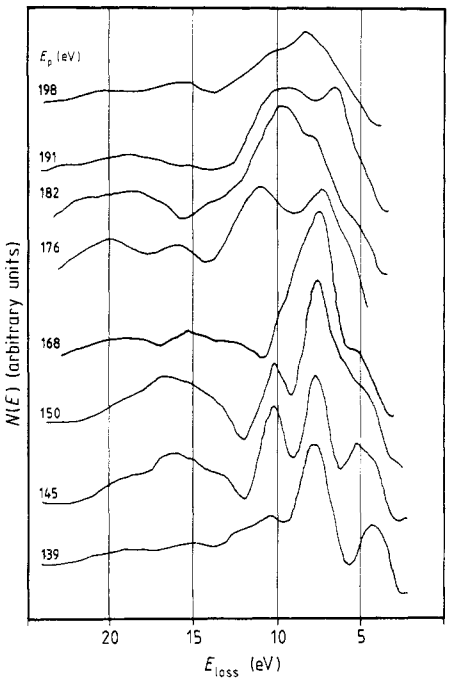

Figure 2. Integral ELS at different primary energies E_p taken at $T \simeq 90$ K.

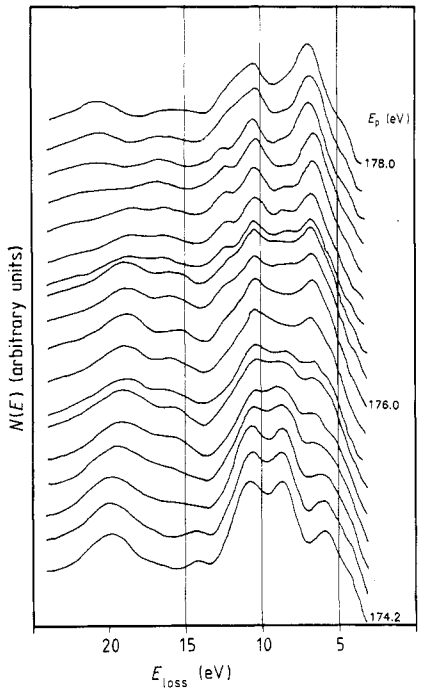

Figure 3. Integral ELS with E_p increased from spectrum to spectrum by $\Delta E_p \simeq 0.2$ eV for $T \simeq 90$ K.

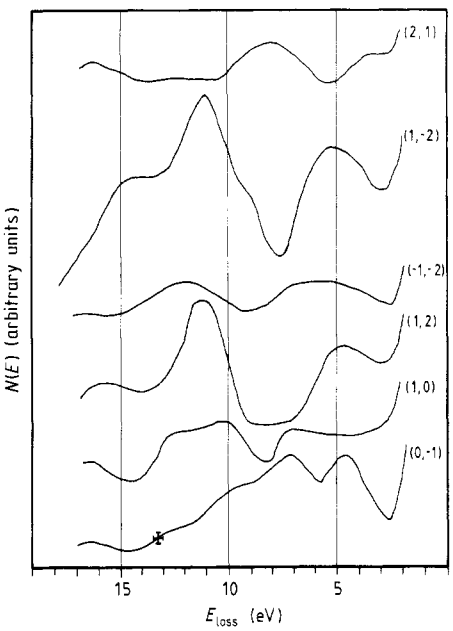

Figure 4. Angle-resolved ELS at $E_p = 174$ eV taken with a spot photometer for $T \simeq 90$ K. The indices of the LEED spots are indicated in parentheses.

For ELS data on a flat Ni(110) surface at room temperature [8, 9, 10] a much less pronounced influence of E_p has been found, showing that our results are clearly related to the existence of ordered steps. The LEED effect alone is apparently not capable of creating such a strong anomaly as observed here (see other examples of flat surfaces—e.g. in [7, 11]). We therefore look for an explanation in the excitation processes. Küppers [9] assigned the loss peak at 8 eV to surface plasmons, whereas Sickafus and Steinrisser [8] interpreted the peak at 8.2 eV as an inter-bank-transition loss. The structure of the complex dielectric constant ε of Ni compiled from optical data [12] indicates the existence of a strong modulation of the free-electron Drude curve by inter-band transitions. In fact, the interpretation of the results of optical measurements on polycrystalline Ni is controversial (see references given in [12]). In view of these results, we cannot assign our observed peaks definitely to surface plasmons, bulk plasmons or inter-band transitions. An additional difficulty arises from the variation of ε [13] as a consequence of a variation in the electronic structure at the surface (see, e.g., [14]) and possibly in the neighbourhood of a step [15, 16]. Displacements of surface atoms at the step edges may also be occurring, reinforcing the effect. As a consequence, we cannot exclude the possibility of finding new electronic states on the present stepped surface.

In spite of these complications we present here a tentative explanation of the observed effect in a simple classical theory using the dielectric model of surface plasmons. In fact, for the additional losses found here there is an analogy to the splitting of the surface plasmon peak of Ag(111) caused by a macroscopic surface roughness [17, 18]. An explanation of the splitting has been given by Kretschmann and co-workers [19] on the basis of a classical model of surface plasmons, using the bulk dielectric constant ε, applied to macroscopically wavy surfaces by Toigo and co-workers [20]. Although we are considering an atomic scale, we apply this theory as a trial, no microscopic theory being available.

For analysing ELS it is convenient to consider the energy-loss function, which has for bulk effects the well known form $P(\omega) = -\mathrm{Im}(1/\varepsilon)$ as a function of energy loss ω. Using the theory from [20] we can derive the energy-loss function for a semi-infinite dielectric material with a wavy surface in the form (for $|\boldsymbol{k}| \gg \omega/c$, $|\boldsymbol{k}'| \gg \omega/c$)

$$P(\omega, \boldsymbol{k}) = -\mathrm{Im}\{[(\varepsilon + 1) - a^2(\varepsilon - 1)^2(\varepsilon + 1)^{-1}]^{-1}\} \tag{1}$$

where

$$a^2 = \sum_{k'} |\boldsymbol{k}|\,|\boldsymbol{k}'|\,|\zeta_{k-k'}|^2(1 - \cos\varphi_{kk'})^2 \tag{2}$$

where $\boldsymbol{k}$ is the wavevector of the surface plasmon lying parallel to the surface, and $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$, $\boldsymbol{G}$ being the reciprocal-lattice vectors of the (in our case one-dimensional) lattice of the periodic surface profile. ζ_G is the Fourier coefficient of the function $\zeta(x)$ representing the periodic surface profile. We choose $\zeta_G = 0$ for $\boldsymbol{G} = 0$. $\varphi_{kk'}$ is the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$. The case $a^2 = 0$ gives the energy-loss function of a flat surface $P(\omega) = -\mathrm{Im}[1/(\varepsilon + 1)]$ [21]. The second term in the square brackets of (1) can be understood to appear as a result of the diffraction of the plasmon wave by the steps. The dispersion relation of surface plasmons for a wavy surface is given by setting the quantity in the square brackets of (1) equal to zero, corresponding to (5.7) of [20].

We have evaluated $P(\omega, \boldsymbol{k})$ given by (1) using the bulk values of ε [12] for different values of a^2 as shown in figure 5. Regarding $|\boldsymbol{k}| \simeq |\boldsymbol{G}|/20$ as a typical value of $|\boldsymbol{k}|$, we estimate, from the geometry of the surface shown in figure 1 the value of a^2 to be around 0.1. We see that a significant deviation from the case where $a^2 = 0$ for a flat surface is

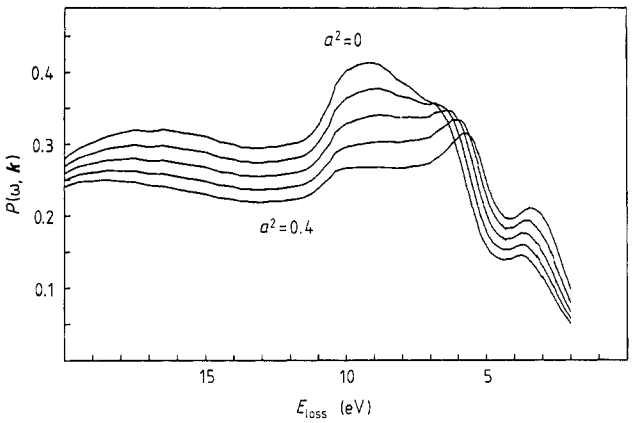

Figure 5. The calculated energy-loss function $P(\omega, \boldsymbol{k})$ for values of a^2 from 0 to 0.4 in steps of 0.1.

obtained. The characteristic variations of spectra found experimentally are apparently introduced by the dependence of the energy-loss function on $\boldsymbol{k}$ through a^2. Due to the LEED effect mentioned above, the operative value of $\boldsymbol{k}$ varies with E_p, is different from spot to spot, and varies significantly in one spectrum with the value of energy loss. For analysing this we need a proper LEED theory. A theory of inelastic scattering including the LEED effect has been developed by Duke and co-workers using a model Hamiltonian for plasmons (see, e.g., [22]) and by Mills and co-workers for surface vibrations (see, e.g., [23]). Obviously in our case the diffraction by the ordered steps should be taken fully into account, making the LEED theory more complicated.

Our calculated results yield only a qualitative explanation of our experiments, of course. A few additional effects, such as the retardation effect [13] for small values of $|\boldsymbol{k}|$, the fact that ε is in reality dependent on $\boldsymbol{k}$ [13], and the Umklapp processes occurring between the surface plasmon and the scattered electron, may be contributing to the large differences between the spectra shown in figure 4. In any case, for a reliable quantitative analysis a microscopic fully quantum-mechanical theory may be required.

As already mentioned, a disorder in the step structure—usually pictured as meandering [1, 2]—could also lead to a roughening transition on our sample of Ni(430) [24]. To find how the disorder influences ELS, we have taken spectra at varying temperatures during cooling of the sample from a sufficiently high temperature. (Heating periods could not be used due to a disturbance by the heating current.) Figure 6 shows a set of integral ELS. Above 400 K the curves resemble those of flat (110) [9]. (We note, however, that in the LEED pattern the out-of-phase spots are still observed above 400 K. They remain detectable at $E_p = 176$ eV up to 480 K. The in-phase spots can be seen up to temperatures higher than 700 K [24].) Weak shoulders appear in the spectra at 370 K. These are fully developed at 260 K. For lower temperatures they become more pronounced. These changes of spectra include two effects. Firstly, phonon scattering takes place increasingly at higher temperatures. It would lead, however, generally only to an overall decrease of intensity, without changing the form of the spectra [25]. Secondly, an onset of a splitting of the 8 eV loss peak in the temperature range $370 > T > 260$ K is clearly due to a rapid decrease of disorder in the step structure with the cooling. At $T > 370$ K the disorder of steps is such that the additional details in ELS disappear. This is explained in our model by the fact that due to a disturbance of the diffraction of the

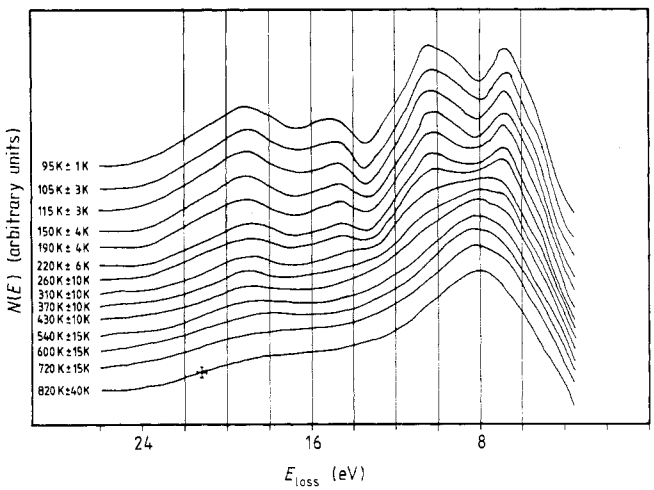

Figure 6. Integral ELS at $E_p = 176$ eV for different temperatures. The decreasing error in T with increasing T is due to the decreasing cooling speed.

plasma wave at the ordered steps the value of the second term in the square brackets of (1) becomes negligibly small. The disturbance can influence only the additional features induced by the ordered steps, so the main peak at 8 eV remains above 370 K. We note that the present effect is apparently more sensitive than LEED intensities to the disordering of steps.

In summary, the anomalous features observed in the ELS of Ni(430) are shown to be particular to the surface having an ordered step structure. Their characteristics are explained by the k-dependent variation of the energy-loss function, caused by the diffraction of the plasma wave by the steps. The variation of the effective value of k is explained by the effect of LEED on the scattered electron. The heating of the sample above 370 K is found to lead to a marked loss of detail in the ELS, verifying their sensitivity to the occurrence of disorder in the step structure.

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