Problem I.S ... X-ray methods 10 points

1. *A layer of iridium* Ir *was sputtered onto a ruthenium* Ru *monocrystal, the process took* 240 min. *The attenuation of the sublayer signal was measured after the deposition using XPS (Al* $K\alpha$*,* $hf = 1486.71\,\mathrm{eV}$*), see the final spectrum in the figure below.*

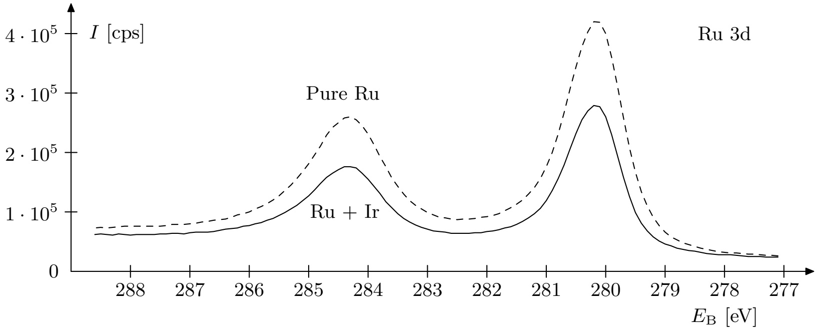

Figure 1: Intensity of the signal from the binding energy of the ruthenium 3d orbital. The dashed line represents the signal before deposition; the solid line is the ruthenium signal after iridium deposition. The unit cps denotes the number of detected electrons per second.

Determine the thickness of the deposited layer of Ir*. Assume that the emission was perpendicular to the surface and the effective photoelectron mean free path in* Ir *is* $\lambda_\mathrm{Ir} = 1.6\,\mathrm{nm}$*. – 4 points*

2. *Consider an iridium sample covered by* 2 nm *thick layer of oxide* $\mathrm{IrO_2}$ *on its surface. Our goal is to study only the active* $\mathrm{IrO_2}$*. This could be achieved by measuring on a synchrotron with the primary photon energy set to* $\approx 150\,\mathrm{eV}$*, such that we would reach the minimum of photoelectron energy as shown on Figure 2.*

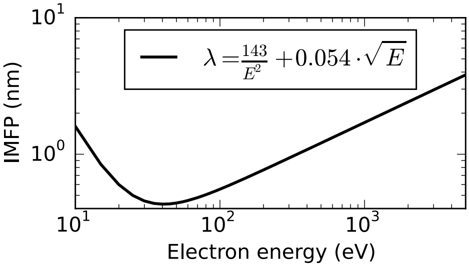

Figure 2: Dependence of the electrons' mean free path λ on the electron energy with an approximate equation for the curve. Both axes are logarithmic.

How could we solve this without a synchrotron? Try to find the specific conditions under which this the result can be reached with X-ray tube capadle of energy 1486.71 eV*, re-*

sulting in the photoelectron mean free path of $\lambda_{\mathrm{IrO}_2} = 3.2\,\mathrm{nm}$. *Does this approach have any disadvantages? – 2 points*

Hint: *Use the formula*

$$I(d) = I_0 \exp\left(-\frac{d}{\lambda\cos\theta}\right)\,.$$

3. *Figure 3 shows a diffractogram of polycrystalline cerium dioxide measured at photon energy of* $77\,\mathrm{keV}$. *To which interplanar spacing do the first 3 maxima correspond to? How do these planes look like in the crystal lattice? And at what angle* 2θ *would we measure them if we used X-ray with energy of* $90\,\mathrm{keV}$*? – 4 points*

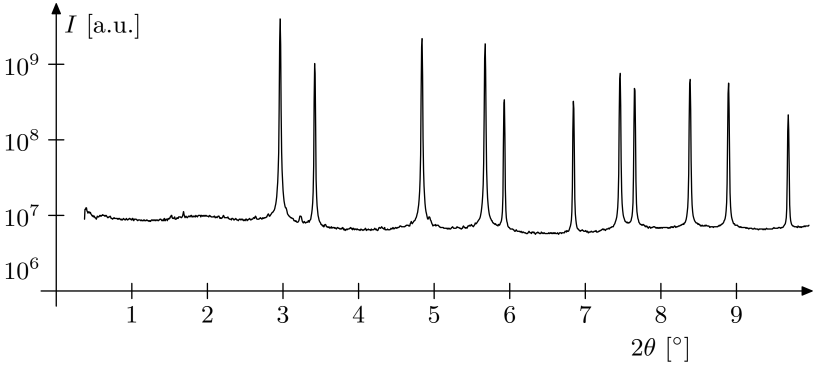

Figure 3: Diffractogram for a powder sample of crystalline cerium dioxide, $\mathrm{CeO_2}$, measured at an X-ray photon energy of $77\,\mathrm{keV}$.

Jarda and Tomáš will irridiate (not irritate!) you right from the beginning.

Notice

In the original statement, the first subproblem was assigned 4 points, the second 2 points, and the third 4 points again. After revising the difficulty of the individual parts, we adjusted the grading of the submitted solutions to the following scheme: 3 points for the first subproblem, 3 points for the second, and 4 points for the third. We believe that this distribution better reflects the actual difficulty of the tasks and we apologize for the change.

Problem 1

Because a layer of iridium was deposited onto ruthenium, photoelectrons emitted from the ruthenium must pass through this layer, where a fraction of them is scattered and therefore does not reach the vacuum or the detector. As a result, the number of detected photoelectrons (i.e. the intensity) is reduced. Since the X-ray radiation that causes photoemission has, in our case, a much larger mean free path than the generated photoelectrons, the presence of the deposited iridium layer has practically no effect on the intensity of the X-ray radiation interacting with the ruthenium. The iridium layer also does not affect the photoemission process itself inside the ruthenium, so the number of photoelectrons emitted from ruthenium perpendicular to the surface is the same before and after the deposition. Let us denote this photoelectron flux by j_0. The detector then measures an intensity (the number of electrons with a given energy) I_0, whose value is directly proportional to the electron flux (some electrons may not be directed toward the detector or may not pass through the analyzer for various reasons, but this should not depend on their total number).

After the deposition of iridium, however, a part of the j_0 electrons is scattered in the deposited layer according to the relation given in the series

$$j = j_0 \exp\left(-\frac{d}{\lambda_{\mathrm{Ir}} \cos\theta}\right) \quad \Rightarrow \quad I \ = I_0 \exp\left(-\frac{d}{\lambda_{\mathrm{Ir}} \cos\theta}\right) \,.$$

According to the problem statement we are to consider normal emission, i.e. perpendicular to the surface, which means $\theta = 0\,^\circ$ and hence $\cos\theta = 1$, so this factor can be neglected in further calculations. If we therefore find the ratio of the ruthenium signal intensities before and after deposition, we can determine the layer thickness d as

$$d = \lambda_{\mathrm{Ir}} \ln\left(\frac{I_0}{I}\right) \,.$$

We thus need to determine the intensities I and I_0 from the graph. One option would be to read off the peak values and compare them. However, due to background, possible noise, or even physical differences between the spectra, this approach may not be the most accurate. The total intensity from a given element is therefore obtained as the area under the curve over the entire region of the two ruthenium peaks.

For improved accuracy, we also subtract the background. There are several theories describing the shape of the background, but a linear approximation is sufficient for our purposes. We therefore determine a line segment connecting the regions at 288 eV and 278 eV, and compute the area under the curve relative to this line segment. This procedure is applied separately to each curve. Since only the ratio of intensities is relevant, arbitrary units of area may be used, provided they are the same for both graphs. The area can be determined, for example, in the program *GeoGebra*, by constructing a polygon that follows the curve and the subtracted background and calculating its area. For the curve before deposition we obtain $I_0 \doteq 13.3\,\mathrm{a.u.}$, and for the second case $I \doteq 8.0\,\mathrm{a.u.}$. Substituting into the expression for d yields the layer thickness

$$d = \lambda_{\mathrm{Ir}} \ln\left(\frac{I_0}{I}\right) \doteq 0.8\,\mathrm{nm} \,.$$

The radiation energy was ultimately not needed, because the mean free path for the given situation was provided directly in the problem. Otherwise, it would have to be obtained from the universal curve corresponding to the photoelectron energy.

Problem 2

In the first part we recalled the relation from the serial

$$I \ = I_0 \exp\left(-\frac{d}{\lambda_{\mathrm{Ir}} \cos\theta}\right) \,.$$

We see that the intensity depends on the angle θ at which the photoelectrons travel within the material and emerge from the sample toward the detector. If electrons pass through a thin layer at an angle rather than perpendicularly, they traverse a larger amount of material and are therefore scattered more strongly.

According to the problem statement, we are to find conditions under which a layer of thickness 2 nm can be studied using laboratory equipment. In other words, we seek the tilt angle required to minimize the signal originating from depths greater than 2 nm. We must choose a threshold that we consider acceptable — due to the exponential attenuation of photoelectron intensities, there is (within our model) no finite depth from which no electrons emerge. We therefore have to choose an acceptable fraction of electrons originating from depths greater than 2 nm. Let us assume, for example, $I_{\mathrm{lim}} = 5\,\%$ of the total intensity I_0, which is already very small and would manifest primarily as noise. Other choices of I_{lim} would also be reasonable, depending on the specific experiment. For this condition we must determine the mean free path of photoelectrons in the synchrotron experiment, λ_{s}, from

$$I_{\mathrm{lim}} = I_0 \exp\left(-\frac{d}{\lambda_{\mathrm{s}}}\right) \quad \Rightarrow \quad \lambda_{\mathrm{s}} = d\left(\ln\left(\frac{I_0}{I_{\mathrm{lim}}}\right)\right)^{-1} ,$$

where d is the thickness of the iridium oxide surface layer.

We would like to achieve the same effective mean free path perpendicular to the surface in our laboratory setup. By tilting the sample, we can project the actual mean free path onto the surface normal and compare the two values,

$$\lambda_{\mathrm{s}} = \lambda_{\mathrm{IrOx}} \cos\theta ,$$

from which we finally obtain the desired angle

$$\theta = \arccos\left(\frac{d}{\lambda_{\mathrm{IrOx}}}\left(\ln\frac{I_0}{I_{\mathrm{lim}}}\right)^{-1}\right) \doteq 78\,^{\circ} ,$$

measured from the normal.

At this angle relative to the surface normal, photoelectrons must be detected so that those originating in the iridium travel a sufficiently long distance within the surface layer and their intensity is sufficiently reduced. We see that the result depends on how many electrons from deeper layers we allow to be detected: we can allow more by a smaller tilt but this results in a larger error, whereas allowing fewer yields higher accuracy at the cost of a much larger tilt. A potential limitation of this approach lies in the technical constraints of the apparatus: the setup must include a translation stage or motor that allows adjustment of the sample orientation, since rotating the analyzer and detector is impractical due to their size and technical complexity.

In addition, tilting the sample and detecting at an angle leads to a significant reduction of the detected signal. Electrons emerge from the material with a cosine angular distribution, meaning that the largest number is emitted perpendicular to the surface, and with increasing angle φ from the normal their number decreases proportionally to $\cos\varphi$. The signal from a thin layer is already weak at normal detection due to the small thickness; while tilting increases its relative contribution compared to the subsurface signal, the total intensity decreases markedly, and the result may still be unsatisfactory. At a synchrotron, in addition to tunable energy, a major advantage is the much higher X-ray intensity and thus a significantly higher signal-to-noise ratio.

Problem 3

The first maximum occurs at an angle $2\theta_1 = 2.96\,^\circ$, the second at $2\theta_2 = 3.42\,^\circ$, and the third at $2\theta_3 = 4.84\,^\circ$. For each case we obtain the angle θ by dividing by two and substitute into Bragg's law,

$$2d\sin\theta = \lambda\,,$$

where the wavelength is also known,

$$\lambda \doteq 0.0161\,\mathrm{nm}\,.$$

This yields the interplanar spacings

$$\begin{aligned} d_1 &= \frac{\lambda}{2\sin\theta_1} \doteq 312\,\mathrm{pm}\,,\\ d_2 &= \frac{\lambda}{2\sin\theta_2} \doteq 270\,\mathrm{pm}\,,\\ d_3 &= \frac{\lambda}{2\sin\theta_3} \doteq 191\,\mathrm{pm}\,. \end{aligned}$$

The lattice constant of cerium oxide is, according to published data, $a \doteq 541\,\mathrm{pm}$, and it crystallizes in a face-centered cubic lattice. We may note that the ratios of the diffracting interplanar spacings to the edge length of the unit cell are

$$\frac{a}{d_1} \doteq \sqrt{3}, \qquad \frac{a}{d_2} \doteq \sqrt{4}, \qquad \frac{a}{d_3} \doteq \sqrt{8}\,.$$

The first corresponds to planes oriented such that they pass through the face diagonals of three mutually perpendicular faces of the cube. The second would correspond to planes parallel to the faces of the unit cell but bisecting the cube. Such planes containing atoms do not exist in the crystal. In reality this is therefore a second-order diffraction ($n = 2$), but Bragg's law describes it using planes so that the order need not be stated explicitly on the wavelength side of the equation. The same applies to the third case—this corresponds to the second order of planes parallel to one edge of the cube, which bisect the perpendicular face along its diagonal. A sketch of these planes is shown in Fig. 4, in the order in which they were just discussed.

If we now apply Bragg's law in reverse and substitute the wavelength $\lambda_2 \doteq 0.013\,8\,\mathrm{nm}$, we obtain the angles $2\Theta_1$, $2\Theta_2$, and $2\Theta_3$ as

$$2\Theta_1 \doteq 2.53\,^\circ\,, \qquad 2\Theta_2 \doteq 2.92\,^\circ\,, \qquad 2\Theta_3 \doteq 4.13\,^\circ\,.$$

At these values, three maxima mentioned in the problem would be observed at this energy.

Comments on the submitted solutions

The first part was almost problem-free; due to the necessity of reading values from a graph, we did not insist on exact numerical values, focusing instead on the procedure. It is, however, always important to state at which energy the intensity values were determined.

In the second part, most of you correctly identified the change of angle during measurement, but the associated disadvantages were less frequently discussed correctly. For example, sample inhomogeneity was often cited as a problem, but the X-ray beam typically has a diameter on the order of tenths of a millimeter, so most samples would not suffer from this issue.

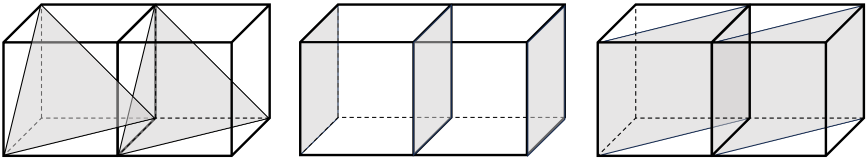

Figure 4: Illustration of the crystal planes responsible for the observed diffraction maxima.

In the third part, determining the exact nature of the diffracting planes proved to be rather difficult, and many participants did not attempt it. This is most easily described using *Miller indices*, which were not introduced in the text of the series in order to keep its length and difficulty at a reasonable level. This is also related to the fact that maxima at higher angles do not necessarily correspond to higher diffraction order, but may arise from differently oriented planes. Without knowledge of Miller indices, it is therefore preferable to assume $n = 1$ and then consider whether planes with the resulting d actually exist in the crystal, or whether a higher order is involved. This is precisely the approach taken in this model solution.

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