

AN INVESTIGATION OF THERMAL VIBRATIONS OF ATOMS ON THE (001) SURFACE OF NICKEL APPLYING THE LOW-ENERGY ELECTRON DIFFRACTION (LEED) METHOD

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Measurements of the temperature dependence of the intensity of various diffracted beams obtained during diffraction of low-energy electrons on the (001) Ni surface were performed for electron energies from 10 to above 500 eV.

The effective Debye temperatures Θ were calculated for the various diffracted beams and for various electron energies E using the slopes of the straight lines $\ln I = f(T)$, found experimentally. The inner potential of the investigated crystal was taken into account in the calculations.

Results of calculations are shown as a curve $\Theta_{\mathbf{h}} = f(E)$. By the extrapolation of this curve to $E = 0$ the surface Debye temperature for the (001) Ni surface is obtained. Its value is 267°K. This is in good agreement with theoretical predictions of Clark, Herman and Wallis (*Phys. Rev.*, **139A**, 860 (1965)). For high electron energies the curve proposed in the present paper approaches the volume Debye temperature for Ni, 410°K, in agreement with that obtained with the X-ray diffraction method.

Introduction

Recently, low-energy electron diffraction became a frequently used tool in studying the phenomena occurring on monocrystalline surfaces and in investigating the nature of the surfaces. Owing to the strong scattering of slow electrons (with energies up to several hundred eV) by atoms of the investigated crystal these electrons do not penetrate appreciably into the lattice of the crystal, hence atoms of the first few layers are responsible for the diffraction effects. Therefore a possibility arises of performing an experiment to provide a comparison of the thermal vibrations of the surface atoms with the corresponding vibrations in the bulk.

The aim of the experiment is to investigate the dependence of the intensity of the diffracted beams on the temperature of the crystal onto which the electrons are scattered. This dependence for X-ray diffraction in a three-dimensional crystal is expressed by the Debye-Waller relation:

$$I = I_0 \exp \{-2W\} \quad (1)$$

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where W is a function of the crystal temperature. If this temperature is not much lower than the Debye temperature of the crystal, W is given by:

$$W = 3\hbar^2 \mathbf{K}^2 T / 2M \sqrt{k} \Theta_{\mathbf{K}}^2 \stackrel{\text{df}}{=} -aT/2 \quad (2)$$

where \mathbf{K} is the scattering vector connected with the investigated diffracted beam and is equal to the remainder of the wave vectors of diffracted and incident beams: $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, M is the mass of each atom of the crystal, k is the Boltzmann constant, $\hbar = h/2\pi$ (h is the Planck constant) and $\Theta_{\mathbf{K}}$ is the Debye temperature connected with the scattering vector and defined as follows:

$$\Theta_{\mathbf{K}} = \hbar \nu_{D,\mathbf{K}} / k \quad (3)$$

$\nu_{D,\mathbf{K}}$ is the top frequency of lattice vibrations in the direction of vector \mathbf{K} in the Debye model. It may be shown that the mean-square displacement of atoms from their equilibrium positions in the direction of vector \mathbf{K} is proportional to the ratio $T/\Theta_{\mathbf{K}}^2$:

$$\langle u_{\mathbf{K}} \rangle^2 = 2W/\mathbf{K}^2 = 3\hbar^2 T / M k \Theta_{\mathbf{K}}^2. \quad (4)$$

The experiment shows that the dependence of the intensity of the diffracted beam on the temperature of the scattering crystal is also characterized by an exponential function in the case of LEED. Consequently, the effective Debye temperature can be introduced in this case and, as was shown in the papers [1, 2] for nickel, in the paper [3] for platinum and in the papers [4, 5] for silver, this temperature is lower than the corresponding bulk value and depends on the energy of the electrons of the incident beam, approaching the bulk value at large electron energies. As the depth of penetration of diffracted electrons also depends on this energy, it may be noted from the results of the above mentioned papers and the relation (4) that the mean-square displacement is larger for surface atoms than that for atoms in the bulk of the crystal.

Investigations of diffracted beams having different orientations of the vector \mathbf{K} in relation to the crystal surface, provides information about the possible anisotropy of thermal vibrations of surface atoms, because each beam gives the information about atoms vibrations in the direction parallel to its vector \mathbf{K} .

The authors of the theoretical paper [6] have presented the calculation of the mean-square displacement of atoms from their equilibrium position in the Ni crystal composed of 20 parallel infinitely extended layers of atoms. The calculations were made for atoms of each of the ten layers separately (counting from the surface) and also separately for vibrations parallel and normal to the crystal surface. The cases in which the free surface was in succession, the (001), (110) and (111) surfaces of Ni monocrystal, were considered. The authors of the mentioned paper found that the mean-square displacement ought to diminish when passing on to deeper and deeper layers, and that this dependence is strong only for the few first layers. It was also found that the spatial anisotropy of this displacement should exist for the surface atoms.

The theoretical predictions contained in the paper [6] are in qualitative agreement with the results of experimental papers [1, 2]. However, quantitative agreement is not sufficient enough. For instance, the authors of the paper [2] have found that the effective Debye

temperatures for the atoms on the (110) Ni surface and for the directions [110], $[\bar{1}\bar{1}0]$ and [001] are equal to 220, 310 and 220°K, respectively. It results from the paper [6] that, as the bulk Debye temperature of Ni equals 410°K, these temperatures should be equal to 286, 322 and 278°K, respectively.

The authors of the paper [3] obtained $\Theta \approx 100^\circ\text{K}$ for atoms on the (001) surface of Pt and for the [001] direction, while, basing on the paper [6] the results of which can be easily adopted to the platinum monocrystal, the value of the effective Debye temperature should be equal to 160°K in this case, if it is assumed that the bulk Debye temperature for Pt is equal to 234°K.

If it is assumed that the bulk Debye temperature for silver is equal to 415°K, the value of the effective Debye temperature resulting from the paper [6] should amount to 150°K for the atoms on the (111) surface of silver and for the direction [111]. For the same case, the value of Θ equal to about 150°K was also found in experimental papers [4, 5]. However, in contrast with the results of the paper [2], the authors of the paper [4] report that they did not find spatial anisotropy of the Debye temperature even though, in their opinion, the accuracy of the measurement was sufficient.

The authors of papers [1-5] make no mention of taking into account the inner potential of the crystal in their calculations.

The aim of the measurements of the present work was to obtain data in order to perform the calculation of the effective Debye temperature for different energies of electrons in the incident beam and for different diffracted beams obtained as a result of the diffraction of low-energy electrons on the (001) surface of the Ni monocrystal. The inner potential of the crystal was taken into consideration in these calculations. The results obtained are in good quantitative agreement with the results of the theoretical paper [6].

Experimental

The measurements were made using a glass, post-acceleration type diffraction camera [7-9] including a filter of the electron energy composed of two spherical grids. The camera is shown in Fig. 1 and its detailed description is given in the paper [10]. After passing through the energy filter, diffracted beams reached the luminescent screen deposited on the inner side of the spherical part of the camera and formed luminous spots on the screen. These spots were observed with the aid of a totally reflecting glass prism provided with a special gap. Using this prism, the spots could be also photographed and photometered.

It was possible to heat the crystal by bombarding it with electrons emitted from a wolfram loop surrounding the crystal. The geometry of the crystal-loop system was such that the electrons could not reach the tested part of the crystal surface. The temperature of the crystal was measured by a Pt-PtRh thermocouple which was spot-welded to the lateral surface of the crystal. The investigated surface of the crystal could be cleaned by bombardment with argon ions. The principle of the method used here is identical to that described in paper [11].

After heating the crystal for several hours to the temperature of about 800°C and after the bombardment of its surface with argon ions, the crystal was moderate (to about 300°C)

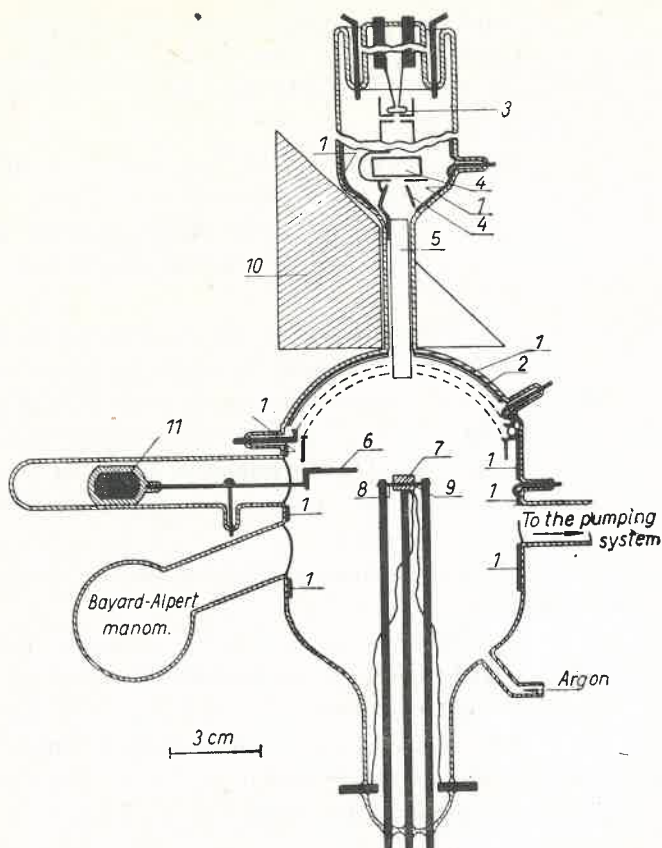


Fig. 1. Diffraction camera. 1 - SnO layer, 2 - the luminescent screen, 3 - the electron gun cathode, 4 - deflection plates of the electron gun, 5 - nickel tube, 6 - shutter for the crystal, moved magnetically, 7 - the nickel crystal, 8 - wolfram loop, 9 - Pt-PtRh thermocouple, 10 - the totally reflecting glass prism, 11 - the iron plug in the glass

heated in order to remove argon atoms stuck into the crystal structure and arrange the damaged surface. The diffraction pattern of the (001) Ni surface obtained after such treatment is shown in Fig. 2.

The vacuum in the diffraction camera was achieved by using a system of two glass diffusion pumps connected in series, operating with silicon oils DC-703 in the first stage and DC-704 in the second stage. Between the camera and pumps a liquid nitrogen trap was placed. The camera was connected through two metal, Bayard-Alpert type vacuum valves produced by the Industrial Institute of Electronics in Warsaw with a container of spectrally clean argon. It was possible to heat the whole of the volume over the trap up to 400°C by a resistance furnace. After outgassing the pumped volume, the trap was constantly cooled with liquid nitrogen and under these conditions the pressure in the pumped volume, measured with the Bayard-Alpert manometer, decreased to $p = 4 \times 10^{-10}$ Tr. The pressure in the camera was probably lower, since nickel was evaporating on its lateral walls during the

outgassing of the crystal and the film of Ni was sorbing the chemically active part of the remaining gases. Under these conditions, after the investigated surface was cleaned, its diffraction pattern remained unchanged for many hours and only after a day and night new weak spots could be observed. These were due to the surface structure formed during adsorption of the remaining gases.

The intensity of the chosen diffracted beams was measured by photometering the spots on the luminescence screen. A spot microphotometer was used for this purpose. In this

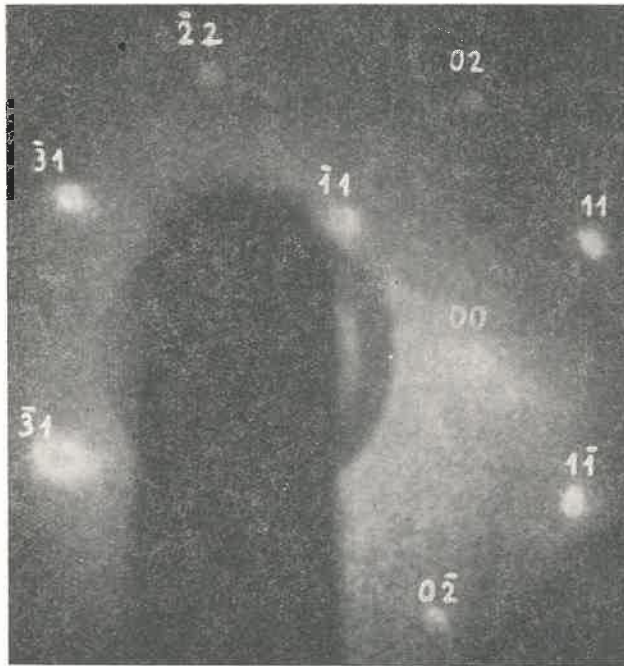


Fig. 2. The diffraction pattern of the clean (001) nickel surface. The background of this pattern is large because of long exposition time in order to show the weak spots as well.

photometer, the light from a chosen spot of the diffraction pattern was directed to the photo-multiplier photo-cathode and the multiplier current was measured.

The crystal was heated to the temperature of 300°C and then, during its spontaneous cooling, the multiplier current was recorded with the aid of an automatic, self-recording compensator. Simultaneously, the temperature of the crystal was measured using the thermocouple. The moments when the temperature reached the chosen values were noted on the record by short-circuit of the compensator input. When the lowest temperature from the measuring interval (50 or 100°C) was reached, the photometer was directed to the point of the screen near the measured spot and the background was recorded. The indications of the recorder at temperatures which had been previously indicated by the short-circuit of the compensator, were read and the background subtracted. It was found from a separate experiment that the background is practically independent of the crystal temperature.

The obtained results were brought together in a table and showed a dependence of the chosen diffracted beam intensity on the crystal temperature.

The measuring system used had to ensure stable conditions during measurements. In particular, it was necessary to ensure the stability of the incident beam intensity, the stability of voltages supplying the electron optics of the diffraction camera and the photomultiplier of the spot microphotometer as well as ensuring the positional invariability of this photometer. The diagram of the measuring system used is shown in Fig. 3. The incident

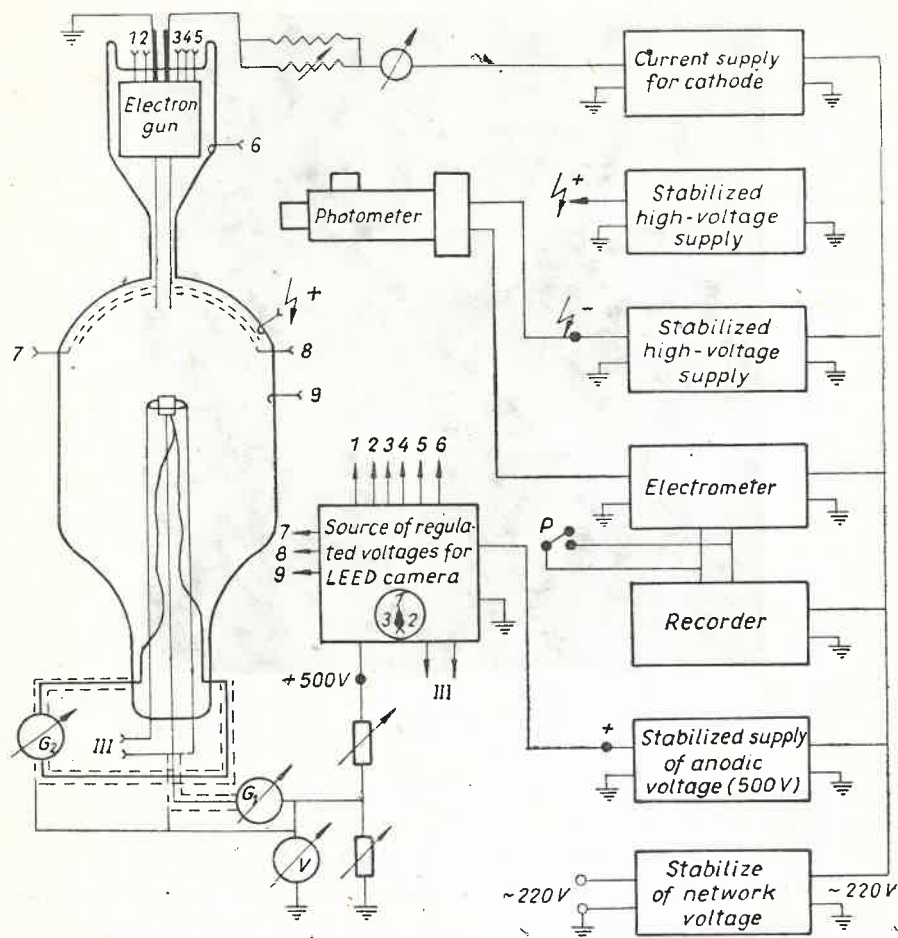


Fig. 3. Diagram of the measuring system

beam stability was controlled by the galvanometer G_1 (Fig. 3). This galvanometer indicated the current flowing from the crystal to its voltage source and was well insulated from the ground among other things its light source was supplied with an inner battery. The stability of readings of this galvanometer was obtained by the regulation the heating current of the electron gun cathode. As it is well-known (see for instance the paper [12]), the secondary

emission coefficient of electrons from metals does not depend significantly on the temperature, thus when the current indicated by the galvanometer was constant, the current of the incident beam was also constant.

The stability of supplying voltages was achieved by using sources with inner electronic stabilization. Apart from this, the sources were connected into the electrical network through a stabilizer of its voltage. In order to provide the invariability of the photometer position, the measurements were made at night to eliminate shocks in the vicinity of the apparatus.

In order to make sure that the precautions taken were sufficient, the measurement was made of the intensity of the chosen diffracted beam at a constant crystal temperature and within a period of time appreciably longer than the time it took to perform individual

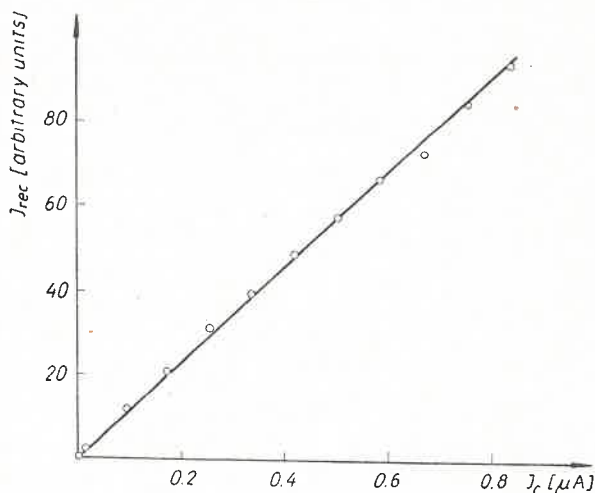


Fig. 4. Result of the linearity test of the measuring system

measurements (the latter was about 6 min.). It was found that data of the self-recording compensator were practically constant during this test.

The proportionality of the self-recording compensator readings to the incident beam intensity was also tested. For this purpose the intensity was changed within a wide range of values and the strong diffraction spot was simultaneously photometered. Fig. 4 shows the obtained dependence of the self-recording compensator readings on the current of the galvanometer G_1 (Fig. 3). As may be seen in this figure, the linearity of the measuring system is quite sufficient.

Results

The results of measurements of the dependence $I = f(T)$ were plotted in the coordinate system $\ln I$ vs T in which this dependence was a straight line. The typical graph of the dependence $\ln I = f(T)$ is shown in Fig. 5. The slope of the straight line was, in agreement with the formulas (1) and (2), equal to:

$$a = -3\hbar^2 K^2 / Mk \Theta_K^2. \quad (5)$$

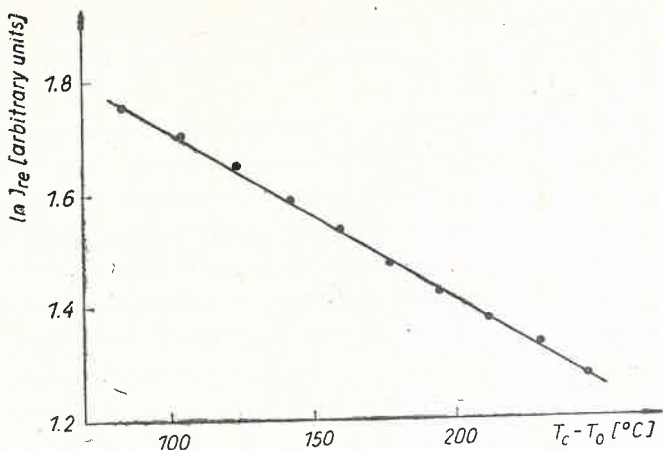


Fig. 5. A typical plot $\ln I = f(T)$ ((00) spot, $E = 291$ eV)

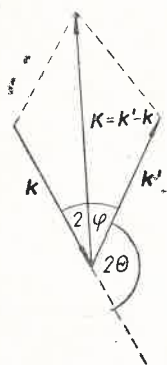


Fig. 6. Relations between k , k' and K vectors

As can be seen in Fig. 6,

$$K^2 = 4k^2 \cos^2 \varphi = 16\pi \cos^2 \varphi / \lambda^2 \quad (6)$$

where λ is the de Broglie wavelength for the diffracted electrons, and may be expressed as follows:

$$\lambda \approx \sqrt{150 / (E + e\Phi_{hk})} \quad (7)$$

where E is the kinetic energy of electrons in vacuum, Φ_{hk} is the inner potential for a chosen diffracted beam and e is the electron charge. λ is given in \AA if E and $e\Phi_{hk}$ are expressed in eV. The estimations done by the author show that the replacement of the inner potentials for the investigated diffracted beams by the inner potential calculated for the (00) beam causes an error in the calculations of Θ_k of no more than 5% at the lowest used energies. As E increases, this error decreases rapidly. Therefore, in the place of Φ_{hk} , Φ_{00} was taken in the calculations of Θ_K for all investigated beams:

$$\Phi_{00} = 16 \text{ eV} / \cos 15^\circ \approx 17 \text{ eV} \quad (8)$$

as the incident angle of the incident beam was about 15° and because the inner potential for nickel is 16 eV (see for instance paper [13]).

$\cos \varphi$ (Fig. 6) may be expressed by the direction cosines of incident and diffracted beams. Direction cosines of the incident beam were determined basing in the analysis of the diffraction pattern of the (001) Ni surface (Fig. 2) obtained during the experiment. The determination was made in the system of coordinates, the axes of which were parallel to the basic vectors of the investigated crystal. Using the well-known formula from the theory of diffraction:

$$\mathbf{k}' = \mathbf{k} + \mathbf{g} \quad (9)$$

where \mathbf{g} is the vector of the reciprocal lattice of the crystal connected with the chosen diffracted beam, the direction cosines of the diffracted beam may be simply expressed in this

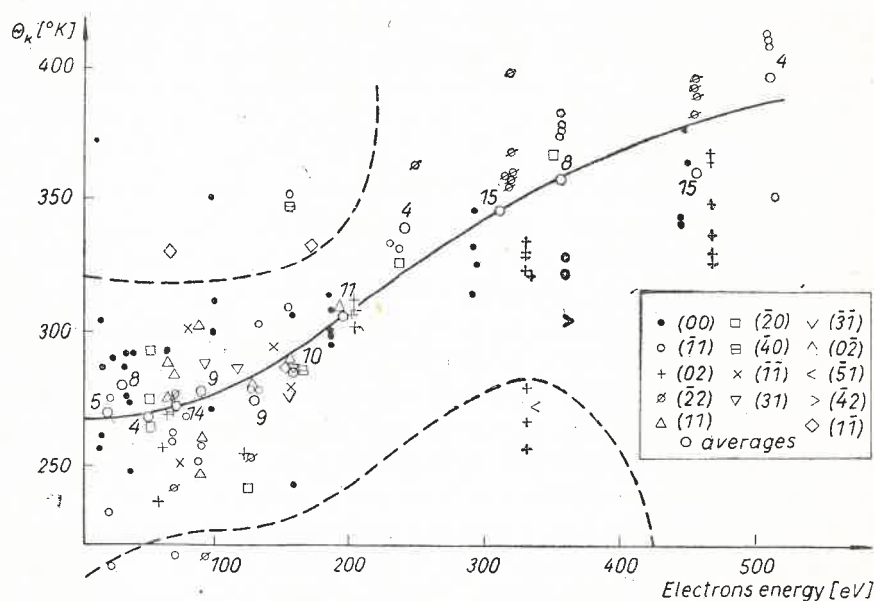


Fig. 7. Diagram of the dependence of Θ_K on the electron energy obtained experimentally

system of coordinates by the direction cosines of the incident beam and the components of the vector \mathbf{g} .

The above method was used to calculate the $\cos \varphi$ for each measurement.

The following expression is obtained for Ni ($M = 9.745 \times 10^{-23}$ g) using the formulas (5), (6) and (7):

$$\Theta_K = \cos \varphi \sqrt{2.615 (E + e\Phi_{hk}) / (-a)}. \quad (10)$$

Inserting the slope " a " found graphically, the value of $\cos \varphi$ and $\Phi_{hk} = 17$ eV (in agreement with formula (8)) in the formula (10) the value of Θ_K may be obtained for the particular measurements.

The values of the Debye temperatures obtained for various electron energies are plotted on the diagram shown in Fig. 7. The large, empty circles on this diagram show the arithmetic means of the experimental points in the particular ranges of electron energies. The number by the circle is the number of experimental points from which the given arithmetic mean value was calculated. The curve of the dependence of $\Theta_{\mathbf{K}}$ vs the electron energy proposed by the author is plotted on this diagram too. The experimental points above the top and below the bottom dashed curves in Fig. 7 were not taken into account in the calculation of mean values.

The surface Debye temperature obtained from the extrapolation of the proposed curve (Fig. 7) to zero electron energy has a value 267°K. Because of a large dispersion of the experimental points in this figure, the accuracy of assessment of the surface Debye temperature is not high. It is seen, however, that it must lie within the range 240–290°K. The detailed discussion of the possible reasons for the dispersion of experimental points can be found in the paper [10]. The obtained results are in good agreement with the predictions of the theoretical paper [6]. The value of $\Theta_{\mathbf{K}}$ calculated in this paper for the (001) Ni surface and for the [001] direction is equal to 280°K, as the bulk Debye temperature of Ni equals 410°K. The experimental points obtained from different diffraction spots, *i.e.* different vectors \mathbf{K} , are placed together on the diagram in Fig. 7. It results from the distribution of these points that no spatial anisotropy of the surface Debye temperature was found. The majority of points are, however, related to the vectors \mathbf{K} which did not form an angle greater than 15° with the normal to the investigated surface. The vectors \mathbf{K} with a greater deviation from this normal were obtained at low electron energies where the accuracy of measurement was not large because of the small slope of the straight line $\ln I = f(T)$.

It results from paper [6] that for the (001) Ni surface the difference between the surface Debye temperatures for the directions normal and parallel to the surface should be about 50°K, therefore for the various investigated spots the effective Debye temperatures obtained at the same electron energies should differ by no more than by twenty °K. With the obtained accuracy of measurements this difference could not be noticed.

The shape of the curve in Fig. 7 is in agreement with the results of papers [14, 15], that electrons with low energies are scattered mainly by the first layer of atoms. Namely, the slope of this curve for electron energies less than 100 eV is negligible. A similar shape of the curve for the (111) surface of silver and for the low electron energies was obtained in the paper [4], while an analogous curves in the paper [3] for platinum and in the paper [5] for the (111) surface of Ag have a large slope just in the range of the lowest electron energies. For higher electron energies the slope of the curve proposed in present paper increases at first and then decreases again at energies approaching 500 eV. This corresponds to deep penetration of electrons in the crystal. The measured effective Debye temperature for this case should approach the volume Debye temperature equal to 410°K, as was obtained for nickel in the paper [16] using the X-ray diffraction method.

The curve in Fig. 7 approaches the volume Debye temperature slower than the corresponding curves for platinum in the paper [3] and for silver in the paper [4], yet with the same speed as the curve for the (111) surface of silver obtained in paper [5]. It has been found experimentally that the diffraction spots due to the surface monoatomic adsorption

layer are noticeable even at electron energies as high as several hundred eV. Therefore it seems that the shape of the curve obtained in the present paper is correct also in its upper part, as even in a highest range of the used electron energies the surface atoms should give a noticeable contribution to the diffraction.

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