

OPTICAL PROPERTIES OF MOLYBDENUM SINGLE CRYSTALS

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The refractive index n and absorption coefficient k are measured in the 0.265–20 micron (4.9–0.06 eV) spectral range for Mo(100). The conduction-electron plasma frequency Ω is determined by infrared measurements and is compared with estimates obtained in the gas approximation. Interband electron transitions in molybdenum are studied in detail. An additional absorption band in the vicinity of 0.5–1.0 eV, which previously had not been observed, is detected on the high-frequency conductivity curve $\sigma(\omega)$. The results are discussed on the basis of available data concerning the energy spectrum of molybdenum.

THE optical properties of molybdenum are of interest in connection with the investigations of its electron structure, since study of the optical absorption gives quantitative information on the structure of the energy bands in the metal.

The optical properties of molybdenum were investigated in a number of studies.^[1-6] It is already known that there exist in molybdenum a very intense absorption band in the region 0.75–5.5 eV,^[1,2] and also low-energy anomalies in absorption, which are connected with spin-orbit splitting of the bands.^[2] Infrared measurements have made it possible to estimate the plasma frequency Ω of the conduction electrons.^[2,6] In the cited investigations, with the exception of^[5], the optical measurements were performed on polycrystalline samples whose surface was prepared by mechanical polishing. It could therefore be assumed that the existence of a cold-working layer exerted a definite influence on the optical characteristics of the molybdenum.

The optical measurements were performed on a single-crystal sample of Mo(100). The dispersion of the complex dielectric constant $\epsilon(\omega)$ was investigated in detail in the spectral region 0.25–20 μ . Particular attention was paid to study of the fine structure on the plot of the high-frequency conductivity $\sigma(\omega)$. The optical data are discussed on the basis of the existing information concerning the energy structure of molybdenum.

SAMPLES, APPARATUS, RESULTS

A molybdenum single crystal ($\rho(4.2^\circ\text{K})/\rho(293^\circ\text{K}) = 10^{-2}$, diameter 12.5 mm, length 120 mm) was grown by the method of electron-beam crucible-free melting. The samples were obtained by cutting the single crystal by the electric-spark method parallel to the (100) face, with accuracy $\pm 2^\circ$. The accuracy of orientation of the face was monitored by x-ray diffraction using the Laue back-reflection method.

After a flat ground surface was obtained, the samples were polished in an electrolyte of the following composition: 68% (by volume) H_3PO_4 + 15% H_2SO_4 + 17% H_2O . The cathode was of stainless steel. The optimal temperature, current, and temporal regimes, which ensured removal of the cold-working layer from

the sample and good specularity of its surface were chosen experimentally. At a current density 0.35 A/cm² and a temperature 60°C different layers of thickness $d \approx 40$ –180 μ were removed from the surface of the sample. The absence of a cold-working layer was also monitored by x-ray diffraction. Topograms obtained from the polished samples by the Schultz method in white radiation have shown that there are no longer any grinding-connected stresses in the sample when a layer $d \approx 80$ –90 μ has been removed. The values of the optical constants were also stabilized when a layer ~ 80 μ was removed. This result agrees well with the data,^[7] where it is shown that the dislocation density in single-crystal molybdenum becomes constant starting with removal of ~ 80 –90 μ of metal. The sufficient volume of the bath and the large distance between electrodes ensured uniform dissolution of the metal over the entire surface of the sample.

It was noted in the measurement process that a few hours after the electric polishing of the sample a weak change is observed in the measured values of ψ and Δ (ψ is the azimuth of the "reconstructed" polarization and Δ is the difference between the phase jumps of the components s and p of the light reflected from the sample), owing to oxidation of the sample. To eliminate this influence, the measurements of the optical constants were carried out on freshly polished samples within 6–8 hours after the instant of polishing.

The refractive index n and the absorption coefficient k were measured by the Beattie polarimetric method.^[8] A description of the apparatus is given in^[2]. For each wavelength λ , 10–12 series of measurements were made. The average values of n and k are listed in Table I. The rms error of the mean value was 2% for n in the region 1–3 μ , 3% in the region 3–20 μ , and for k the error was 1–2% in the region 1–5 μ and 2–6% in the region 5–20 μ . From the obtained values of n and k , we calculated the real part $\epsilon_1(\omega) = n^2(\omega) - k^2(\omega)$ and the imaginary part $\epsilon_2(\omega) = 2n(\omega)k(\omega)$ of the dielectric constant of the molybdenum, the high-frequency conductivity $\sigma(\omega) = n(\omega)k(\omega)\omega/2\pi$ and the reflectivity $R(\omega)$ (ω —circular frequency of the light wave).

Figure 1 shows the results obtained for R in the present paper, and also in^[3,4], where the measurements were carried out in the visible and ultraviolet

Table I

λ, μ	n	k									
0.265	1.43	3.57	1.00	2.62	4.08	2.9	2.54	14.1	7.50	7.33	34.9
0.280	1.82	3.72	1.10	2.28	4.75	3.0	2.70	14.9	7.75	7.75	35.8
0.289	1.94	3.76	1.20	1.99	5.26	3.1	2.65	15.3	8.00	8.25	37.8
0.302	2.21	3.56	1.25	1.89	5.50	3.2	2.60	16.0	8.25	8.20	37.3
0.312	2.14	3.61	1.30	2.00	6.08	3.3	2.74	16.2	8.50	9.35	39.4
0.365	2.65	3.50	1.35	2.23	6.37	3.4	3.03	16.5	8.75	9.93	39.5
0.404	2.66	3.41	1.40	2.20	6.66	3.5	2.90	17.5	9.00	9.73	40.6
0.425	2.71	3.41	1.45	2.17	6.86	3.6	2.90	17.7	9.25	10.1	41.2
0.450	2.84	3.31	1.50	2.13	7.27	3.7	3.25	18.2	9.50	10.1	41.2
0.475	2.95	3.64	1.55	2.10	7.45	3.8	3.50	18.6	9.75	10.3	42.5
0.500	3.15	3.73	1.60	2.16	7.83	3.9	3.60	19.0	10.0	11.0	43.9
0.525	3.22	3.74	1.65	2.12	8.15	4.0	3.47	19.4	10.5	12.4	47.4
0.550	3.47	3.56	1.70	2.09	8.58	4.1	3.38	20.4	11.0	13.5	49.4
0.575	3.42	3.55	1.75	2.02	8.79	4.2	3.50	21.1	11.5	13.2	50.5
0.600	3.38	3.56	1.80	2.00	9.08	4.4	3.60	21.7	12.0	15.5	52.0
0.650	3.45	3.67	1.90	1.85	9.80	4.5	3.70	22.1	13.0	17.0	55.2
0.675	3.47	3.74	2.0	1.80	10.4	4.75	4.10	22.8	14.0	19.7	57.1
0.700	3.48	3.70	2.1	1.80	10.6	5.00	4.25	23.9	15.0	21.1	60.5
0.725	3.50	3.80	2.2	1.75	10.7	5.25	4.60	25.0	16.0	22.6	63.5
0.750	3.52	3.65	2.3	1.67	11.6	5.50	4.76	26.1	17.0	24.3	67.9
0.775	3.47	3.57	2.4	1.76	11.7	5.75	5.12	27.0	18.0	27.0	71.0
0.800	3.46	3.65	2.5	2.10	12.6	6.50	6.00	30.4	19.0	30.7	74.0
0.850	3.29	3.58	2.6	2.35	13.1	6.75	6.10	31.6	20.0	34.0	78.0
0.900	3.04	3.67	2.7	2.43	13.5	7.00	6.40	32.7			
0.950	2.84	3.85	2.8	2.45	13.7	7.25	6.50	33.6			



FIG. 1. Reflectivity of molybdenum is given by different workers. \circ —Mo(100), present paper, dashed—mechanically polished (MP) sample [1,2]; \times —MP sample annealed in vacuum 10^{-7} mm Hg at $T = 2200^\circ\text{K}$ [3]; \bullet —MP sample annealed in vacuum [4].

regions of the spectrum on mechanically polished polycrystalline samples subjected to high-temperature annealing in a vacuum of 10^{-7} mm Hg. The figure also shows the values of R calculated from the optical constants n and k pertaining to molybdenum samples with mechanically polished surface. [1,2] A comparison of the different data shows that our results on Mo(100) agree qualitatively with the available optical data on molybdenum in the infrared, visible and ultraviolet regions of the spectrum, with the exception of the region 1.2 – 2.5μ , in which an additional absorption band was clearly revealed in the case of the single crystal (see Fig. 5 band (a), below). It should also be noted that electric polishing of the sample surface caused the absolute values of n and k for Mo(100) to increase by 10–20% compared with the corresponding data for mechanically polished polycrystalline molybdenum, [1,2] especially in the infrared region.

DISCUSSION OF RESULTS

A. Intraband electron transitions. In the optical frequency band, at room temperatures, the real and imaginary parts of the dielectric constant of the metal are described by the relations

$$\begin{aligned}
 -\epsilon_1(\omega) &= \epsilon_1(\omega) + \frac{\Omega^2}{\omega^2 + \gamma^2} + \epsilon_1'(\omega), \\
 \epsilon_2(\omega) &= \epsilon_2(\omega) + \frac{\Omega^2\gamma}{(\omega^2 + \gamma^2)\omega} + \epsilon_2'(\omega),
 \end{aligned}
 \quad (1)$$

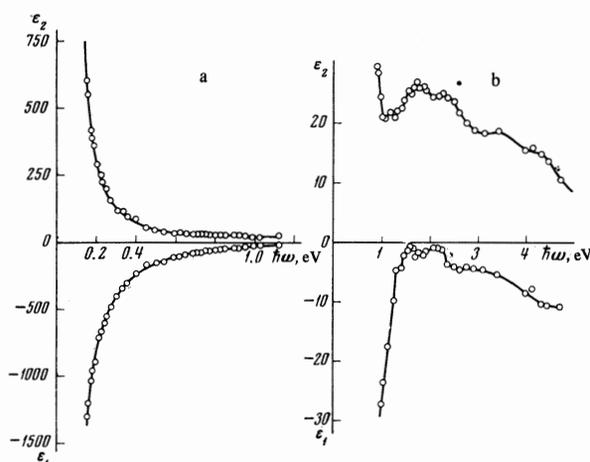


FIG. 2. Dispersion $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ of Mo(100).

Ω and γ are the plasma and relaxation frequencies of the main group of conduction electrons ($\gamma \leq \omega$); $\epsilon_1'(\omega)$ and $\epsilon_2'(\omega)$ are the contributions from the rapidly-relaxing conduction electrons ($\gamma > \omega$), the presence of which in $\epsilon(\omega)$ is a characteristic feature of transition d metals; $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the contributions from the interband transitions.

The contribution from the intraband transitions to $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ decreases in absolute magnitude with increasing ω . As shown by Fig. 2, the $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ of molybdenum change monotonically with the frequency of the light in the spectrum interval 5 – 19μ , thus indicating that intraband electron acceleration plays a decisive role in this region of the spectrum. Assuming that in this region we have $\epsilon_2(\omega) = 0$ and $\epsilon_1(\omega) + \epsilon_1'(\omega) = P$, we determine the values of Ω and γ for Mo(100) from relations (1), using the scheme previously applied to tungsten. [9] The Argand diagram, which represents the dependence of the high-frequency conductivity $\sigma(\omega)$ on the dielectric constant $\epsilon_1(\omega)$ is represented in the spectral region 7 – 19μ by a straight line (Fig. 3), the slope of which yields $\gamma = 0.84 \times 10^{14} \text{ sec}^{-1}$. From the slope and segment of the line $1 - \epsilon_1(\omega) = f(\omega^2 + \gamma^2)^{-1}$ at $\gamma = 0.84 \times 10^{14} \text{ sec}^{-1}$ we obtain the square of the

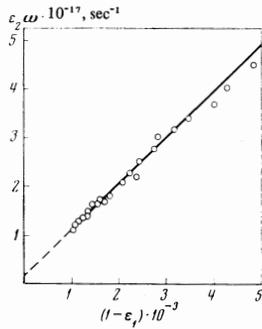


FIG. 3. Argand diagram of Mo(100).

Sample	$\Omega_{\text{opt}}^2 \cdot 10^{30}, \text{sec}^{-2}$	$\Omega_{\text{calc}}^2 \cdot 10^{30}, \text{sec}^{-2}$
Mo(100), electric polishing	77 (present work)	120 ($S_F = 24.1 \text{ \AA}^{-2}$ [13])
Mo, mechanical polishing	79 [2] 85 [9]	150 ($S_F = 27 \text{ \AA}^{-2}$ [15])

plasma frequency $\Omega^2 = (77 \pm 7) \times 10^{30} \text{ sec}^{-2}$ and $P = 250$. We note that although the contribution of the interband transitions to the polarizability seems large ($P = 250$), in the spectrum interval $19-7 \mu$ it amounts to only 5–14% of the experimental value of $\epsilon_1(\omega)$. The parameters of the straight lines were determined by least squares.

Table II lists the values of Ω_{opt}^2 pertaining to different molybdenum samples. We note that the discrepancy between the results is small ($\sim 10\%$). It is of interest to compare the square of the plasma frequency obtained from optical measurements with the estimates of Ω^2 in the model of an ideal Fermi gas with arbitrary dispersion law. It is known that, knowing the total area of the Fermi surface S_F and the density of states on the Fermi level, it is possible to estimate the lower limiting value of the square of the plasma frequency of the metal in the gas approximation. A description of the sequence of the calculation is given in [6, 9].

The density of states on the Fermi level $G(E_F)$ was determined in molybdenum with allowance for the electron-phonon renormalization from the expression [10]

$$G(E_F) = 3\gamma_0/\pi^2 k^2 \frac{d}{A} (1 + \lambda_0), \quad (2)$$

where γ_0 is the experimental value of the temperature coefficient of the electronic specific heat, [14] and λ_0 is the constant of the electron-phonon interaction. The parameter λ_0 , according to Hopfield [11] was calculated from the relation $\lambda_0 = \hbar\gamma_{\text{opt}}/2\pi kT$, where γ_{opt} is the frequency of the electron-phonon scattering of the conduction electrons, determined from optical infrared measurements. For a single-crystal molybdenum sample, we have $\gamma_{\text{opt}} = 0.84 \times 10^{14} \text{ sec}^{-1}$ (determined above) and $\lambda_0 = 0.35$.

The total area of the Fermi surface of molybdenum, according to the data of Loucks, [12] is 23.9 \AA^{-2} . A closely similar value, $S_F = 24.1 \text{ \AA}^{-2}$, was obtained by Boiko et al. [13] from measurements of the radio-frequency size effect. Sparlin and Marcus [15] determined S_F with the aid of the de Haas-van Alphen effect and found it to be 27 \AA^{-2} . The numerical estimates of Ω^2 obtained in the gas approximation for two values of S_F differ no-

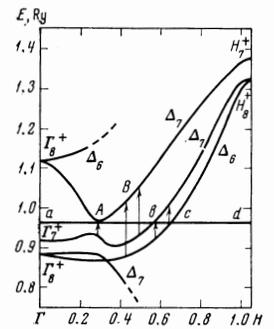


FIG. 4. Relativistic energy bands of tungsten in the ΓH direction of the Brillouin zone [20]. The arrows denote the gaps between bands 4–5 (A), 3–5, 4–5 (B), and 3–4.

ticeably (see Table II), but in both cases Ω_{gas}^2 is much larger than the experimental values of Ω_{opt}^2 . If it is recognized that according to [16] the plasma frequency is sensitive to the correlation interaction of the electrons, then the discrepancy between Ω_{opt}^2 and Ω_{gas}^2 gives grounds for assuming that the effects of the electron correlation in molybdenum are quite noticeable. This result is in agreement with the conclusion of [6].

B. Interband transitions of electrons. The optical absorption in the region of interband transitions is determined by the singularities of the structure of the energy spectrum of the metal in k -space and the values of the interband gaps at different points of the Brillouin zone.

The band structure of molybdenum is similar in many respects to the band structure of tungsten. According to calculation, [12, 17] the two lower energy bands in molybdenum and tungsten are filled, and bands 3, 4, and 5 are occupied—respectively 1.77, 0.18, and 0.05 eI/at (for molybdenum) and 1.76 and 0.24 eI/at (for tungsten). [15] The five band space in tungsten is not occupied. As a result of the spin-orbit interaction, gaps between the three and four and four and five bands appear in the energy spectra of molybdenum and tungsten. Their values were determined experimentally, [13, 18] and were also calculated theoretically for tungsten. [19, 20] The relativistic energy bands of tungsten in the ΓH direction of the Brillouin zone [20] are shown in Fig. 4.

The optical absorption spectrum of molybdenum and its energy structure were already compared earlier. [2] The intervals of allowed interband transitions were estimated and it was shown that the placement of the principal absorption band in molybdenum in the spectral interval 1–5.5 eV is connected with electron transitions between bands 3–4, 3–5, and 4–6, the largest contribution to the absorption being made by transitions between bands 3 and 4, since they are allowed at all points and in all directions of the Brillouin zone. All the estimates were based on the results of Mattheiss, [17] using the calculation of the energy spectrum of tungsten performed in the nonrelativistic approximation. The basis for this was the calculations of Loucks, [12] which have shown that in the nonrelativistic case the Fermi surfaces of molybdenum and tungsten are identical, and the band widths are equal. Since no new calculations of the energy spectrum or theoretical calculations of $\sigma(\omega)_{\text{opt}}$ have recently been performed for molybdenum, there is nothing to be added to the interpretation given for its principal absorption band in [2].

In addition to the already mentioned exceedingly in-

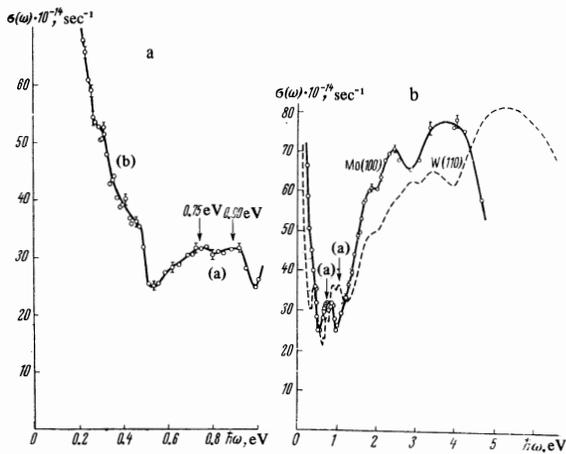


FIG. 5. Dispersion of $\sigma(\omega)$ of molybdenum. The dashed curve represents $\sigma(\omega)$ of tungsten in accordance with the data of [9].

tense band ($\hbar\omega = 1-5.5$ eV), one can note in the absorption spectrum of molybdenum (Fig. 5) a narrow absorption band (a) in the region 0.5–1 eV, which was distinctly revealed by the present measurements. The $\sigma(\omega)$ curve also exhibits nonmonotonocities at energies 0.14–0.17 eV¹⁾ and an inflection (b) in the region 0.2–0.4 eV (Fig. 5a).

Let us turn to consider the nature of the low-energy transitions in molybdenum. With the aid of the size effect it has been shown that in the ΓH direction of the Brillouin zone the bands 3 and 4 are separated by a gap (Fig. 4), which in molybdenum amounts to 2.5% of the distance ΓH ,^[13] and in tungsten to 5%.^[18] According to approximate estimates of Sparlin and Marcus,^[15] the gap between bands 4 and 5 (lens-neck of the "jack") amounts to ~ 0.1 eV for molybdenum and ~ 0.3 eV for tungsten. In tungsten, these gaps were observed in an optical experiment^[9] at energies 0.3–0.4 eV. As to molybdenum, band 5 in the energy spectrum is partly filled and its bottom lies somewhat lower than the Fermi level, and therefore the minimum energy gap between bands 4 and 5, estimated by the authors of [15] at 0.1 eV, is not reflected in the optical absorption spectrum. The $\sigma(\omega)$ curve reveals bursts at energies $\hbar\omega > 1$ eV, due to allowed transitions of the electrons from the occupied states of band 4 to the free states of band 5 above the Fermi level. These transitions will not make a large contribution to $\sigma(\omega)$, since they proceed in a very limited volume of the Brillouin zone. Indeed, weak interband transitions are observed in molybdenum in the region 0.25–0.5 eV, and cause a small inflection (b) on the $\sigma(\omega)$ curve (Fig. 5a).

The dispersion of $\sigma(\omega)$ also reveals nonmonotonocities in the region 0.14–0.17 eV; their presence in the absorption spectrum of molybdenum was noted by us earlier.^[2] However, contrary to expectations, these singularities did not become more clearly pronounced in measurements on a single-crystal sample. Their appearance in the optical spectrum may be connected with

spin-orbit splitting of bands 3 and 4 in molybdenum (transitions in the region bc, Fig. 4), but more convincing experimental proof of their existence is necessary, for example, measurements of the optical conductivity at low temperatures or study of the spectra of thermal reflection and piezoreflection.

Let us examine the narrow absorption band (a) in molybdenum in the region 0.5–1 eV (Fig. 5a). The band is resolved into two peaks, separated by an energy $\Delta E \approx 0.15$ eV. We attribute its occurrence to (s-d) transitions between bands 3–5 and 4–5 at the points $\Delta(4, 0, 0)$, $\Delta(5, 0, 0)$, and $\Delta(6, 0, 0)$ of the Brillouin zone (Fig. 4, transition B). It can be assumed that the distance between the peaks determines approximately the gap between bands 3 and 4. It is interesting to note that the optical spectrum of tungsten has an analogous band (a) (Fig. 5b). The indicated band in tungsten is shifted towards higher energies, and this is evidence that the energy gaps between the corresponding bands in the spectrum of tungsten are larger than in the spectrum of molybdenum.

The noted quantitative similarity of the absorption spectra of molybdenum and tungsten confirms the calculated data^[12] on the similarity of the energy spectra of these metals. Relativistic effects lead to an increase of the width of the energy bands in the metal. This results in a noticeable broadening of the principal absorption band of tungsten compared with the analogous absorption band in molybdenum. This regularity was already noted by us in [9].

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¹⁾The values of $\sigma(\omega)$ in this energy interval are not shown in Fig. 5a. However, the presence of these singularities in the dispersion of $\sigma(\omega)$ is confirmed by the nonmonotonic variation of n and k with increasing λ (see Table I).

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