Temperature dependence of the optical properties and the energy spectrum of zinc

R. G. Yarovaya, I. N. Shklyarevskiĭ, and A. F. A. El-Shazly

Khar'kov State University

(Submitted February 3, 1973)
Zh. Eksp. Teor. Fiz. 65, 673–679 (August 1973)

The optical constants of single-crystal zinc at $E \perp c$ at 290°K and the reflection coefficient at 90, 290, and 630°K are measured in the 0.4–2.3-μ spectral range. The existence of two absorption peaks is observed. The 1.9-μ peak, which has not been observed previously, is ascribed to an interband transition near the *K* point. The oscillator strengths of the interband transitions are determined and the influence of oxidation of the specimen on the optical properties is taken into account. The temperature dependence of the reflection at $\lambda < 0.8$ μ is opposite to that previously observed [3] but is consistent with the theoretical predictions.[6]

A comparison of the experimentally observed peaks of optical absorption in spectra of metals with definite interband transitions makes it possible to refine the theoretical calculations of the energy spectrum. Such an identification, if based only on the position of the absorption band in the spectrum, can frequently be ambiguous. A more reliable interpretation is afforded by an analysis of the selection rules and allowance for optical anisotropy in the case of noncubic structures; the experiment should be performed with single-crystal samples. Further refinements can be made by investigating the temperature variations in the spectrum. Unfortunately, the temperature dependences of the optical characteristics of metals have been little investigated, owing to the serious experimental difficulties.

From the point of view of all the indicated factors, zinc is one of the most thoroughly studied metals. There are at least four modern investigations of the optical properties of this metal, three[1–3] devoted to single-crystal zinc in the interband absorption region, with data at liquid-nitrogen and room temperatures obtained in[2,3], and one[4] devoted to polycrystalline samples in the infrared. Detailed calculations of the energy band structure of zinc at T = 0° K[5] have been tied-in with all the experimental investigations of the properties of the Fermi surface, and predictions on the character of the temperature dependence of the optical absorption were made on the basis of a theoretical analysis of the temperature changes occurring in the energy spectrum[6]. However, some discrepancies between the results of different studies, disparity between experiment and theory, and insufficient degree of study of some fine details of the optical characteristics have induced us to continue the study of the optical properties of zinc.

EXPERIMENTAL TECHNIQUE AND MEASUREMENT RESULTS

Since the largest temperature effect is expected for $\mathbf{E} \perp \mathbf{c}$, and other data of interest to us pertain primarily to this polarization, the samples used to study the optical properties of zinc were crystals grown by the Bridgman method, cooled in liquid nitrogen, and cleaved along the (0001) plane. The initial zinc of ChDA ("pure for analysis") grade was purified further by multiple recrystallization. Immediately after cleaving, the crystals were immersed in ethyl alcohol, where they were kept until room temperature was reached. We preferred to confine ourselves to a study of the basal plane, since all methods of cutting and polishing crystals lead inevitably to the appearance of scattering and surface transition layers, which are difficult to account for.

TABLE I. Optical constants of zinc single crystals ($\mathbf{E} \perp \mathbf{c}$)

λ, μ	Measured		Calculated with correction for oxidation		λ, μ	Measured		Calculated with correction for oxidation	
	n	*h*	*n*	*k*		*n*	*h*	*n*	*k*
0,397	0,54	3,56	0.63	4,01	0.880	5.11	3.40	—	—
0,425	0,69	3,87	0.83	4,36	0.900	5.07	3.07	5.40	2.90
0,452	0,82	4.06	1.03	4.55	0.928	5.62	2.85	—	—
0.480	0.97	4,36	1,18	4.85	0.950	4.27	2.56	—	—
0,507	1.07	4.52	1.30	5.01	0.975	4.00	2.39	—	—
0,532	1,34	4.83	1.61	5.27	0.995	3.43	2.22	3.54	2.16
0.554	1,60	5.11	1.92	5.63	1,027	2.94	2.32	—	—
0,578	2,01	5.21	2,41	5.74	1,055	2.53	2,37	—	—
0,610	2.72	5.45	3,37	5,84	1.160	1,57	3.86	1.65	3.96
0,631	2,93	5.36	3.54	5.70	1.300	1,44	5.23	1,48	5,29
0,660	3,48	5,43	4,10	5.73	1,375	1,23	5.40	—	—
0,675	3.73	5,45	—	—	1.450	1,31	6.42	1.40	6.73
0.685	3.89	5.53	—	—	1.507	1.36	6.56	1.46	6.89
0,700	3,95	5.31	4,57	5.49	1.550	1.51	7.11	1.63	7.36
0,720	4,13	5,31	—	—	1,607	1.60	7.65	1.73	7.94
0,738	4.48	5.28	4.75	5.48	1,660	1,66	7,90	1,77	8.14
0.757	4.54	5,18	—	—	1.750	1.72	8.32	1.84	8.50
0.775	4.75	5.05	5,10	5.24	1,852	2.06	9.42	2.20	9.70
0.800	4,88	4,65	5,40	4,83	1,940	2.03	9.77	2.20	10,15
0,815	5,04	4,62	—	—	2,050	1,89	9.76	2,07	10.24
0,833	5,12	3,98	—	—	2,140	1.80	10.15	1.96	10.58
0,863	5.06	3.77	—	—	2.230	2.00	11.09	2,08	11,56

The optical constants n and k in the 0.4–2.3 μ range were measured at T = 280° K by the Beattie method[7], at incident-light angles 70°–80°, using a ZMR-2 monochromator. Although the investigated plane of the crystal is isotropic, its interaction with the crystal when the light is obliquely incident should, strictly speaking, be expressed in terms of the two principal values $\epsilon_\parallel$ and $\epsilon_\perp$ of the dielectric tensor. From an earlier analysis[8], however, it follows that the influence of $\epsilon_\parallel$ on the results can be neglected in practice at the optical-constant values of zinc in the investigated spectral region. The measurements and calculations for the (0001) plane of zinc single crystals were therefore made as if the sample were isotropic; the obtained optical constants could be regarded as connected with $\epsilon_\perp$ by the relation

$$\sqrt{\varepsilon_\perp} = n - ik.$$

They were determined with accuracy 2–5%. The results of these measurements are listed in Table I.

The reflection coefficients R_r at room temperature were measured relative to an aluminum or silver mirror with the same setup, and for $\lambda < 1.1$ μ they were measured with an SF-4 spectrophotometer by the method of[9]. The measured values of R_r agreed with those calculated from the optical constants within 1% throughout, with the exception of two sections of the spectrum.

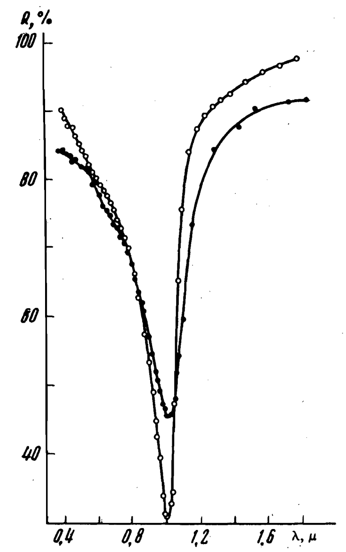


FIG. 1. Dispersion of the reflection coefficient of single-crystal zinc: O–T = 290°K; O–T = 90°K.

In the minimum-reflection region, it was necessary to use wider slits in the SF-4 spectrophotometer, so that the measured R_r exceed the calculated ones by 2–3%. The 2–4% difference in the 0.62–0.7 μ region is apparently due to the lower measurement accuracy resulting from the use of a different radiation receiver.

To measure the low-temperature reflection R_L, the sample and the silver standard were mounted on a copper holder cooled by liquid nitrogen in a cryostat equipped with a carbon absorption pump and a quartz window for the optical measurements. No changes of R_L attributable to condensation of vapor on the sample surface were observed after prolonged cooling. The cryostat was placed either between the exit slit and the ZMR-2 radiation receiver, or on a special attachment of the SF-4 instrument[10]. The reflection coefficient R_L was measured by two methods. In the first we measured the ratio of the reflected intensities I_{sa} and I_{st} of the sample and of the standard before and after cooling. Then

$$R_L = \frac{(I_{sa}/I_{st})_L}{(I_{sa}/I_{st})_r} R_r.$$

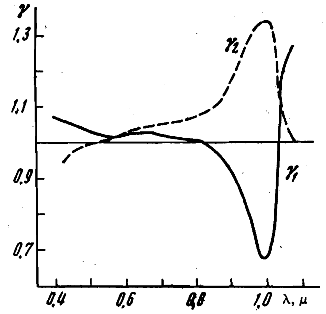
In the second method, the ZMR-2 instrument automatically recorded the $(I_{sa})_r$ and $(I_{sa})_L$ spectra. In this case

$$R_L = [(I_{sa})_L/(I_{sa})_r] R_r.$$

The results obtained by both methods coincided and their mean values are shown in Fig. 1. The error in R_L did not exceed 2%.

We note that in accordance with[11,12] the reflection coefficient of silver at $\lambda > 0.6$ μ is practically independent of the temperature. The measurement results at $\lambda > 0.6$ μ were subjected to slight corrections. According to our data, the minimum reflection at room temperature is 7% lower than in[3], and the reflection at short wavelengths is 3–4% lower. The discrepancies are still larger in the low-temperature measurements. According to Rubloff[3], at $\lambda < 1$ μ low-temperature reflection is always at least 10% lower than at room temperature. In our case, at $\lambda < 0.8$ μ, we obtain $R_L > R_r$ (by 5% at $\lambda = 0.4$ μ). Such discrepancies cannot be attributed to differences in the experimental conditions or in the properties of the samples.

FIG. 2. Spectral dependences of $\gamma_1 = R_L/R_r$ and $\gamma_2 = R_H/R_r$.



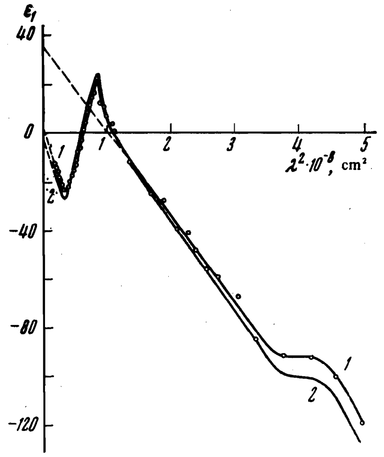


FIG. 3. Plot of $\epsilon_1(\lambda^2)$ of single-crystal zinc: 1–without allowance for oxidation; 2–with allowance for oxidation. Dashed line–extrapolation of linear sections.

Since the signs of the temperature changes at small λ are very important for comparison with theory, we measured also the reflection coefficient R_H of zinc heated to 630° K. The method of determining R_H is similar to that used to find R_L. To avoid oxidation, a thin layer of quartz was deposited on the surface of the sample in vacuum. After many hours of heating, the value of R_r of such a sample remained unchanged. When this measurement method is used, R_H characterizes the reflection from the interface between the zinc and the quartz film, and it cannot be quantitatively compared with the value of R_L at a zinc-air interface. However, the sign of the ratio R_H/R_r does not depend on the properties of the second medium, since the thickness and refractive index of the quartz layer depends very little on the temperature.

From Fig. 2, which shows the spectral dependences of $\gamma_1 = R_L/R_r$ and $\gamma_2 = R_H/R_r$, it follows that measurements performed at low and high temperatures give identical results. The reflection in the region of the short-wave slope of the investigated absorption band increases with decreasing temperature.

DISCUSSION OF RESULTS

Figures 3 and 4 show the dispersions of the real and imaginary parts of the dielectric constant calculated from the optical constants. The principal absorption band, which is connected with interband transitions in the HL direction in the Brillouin zone, has a maximum at $\lambda = 0.725$ μ. The small singularity on the high-frequency slope (Fig. 4) corresponds apparently to the second maximum predicted[6] for transitions near the L point. Just as in the earlier experiments, we observed a much

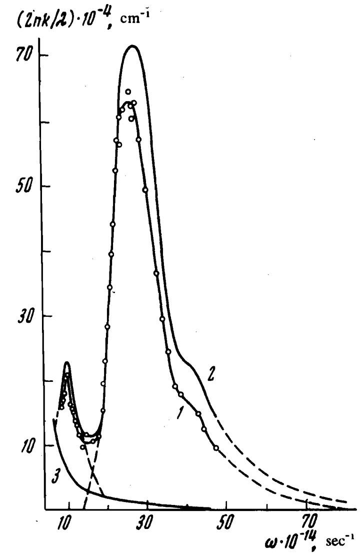


FIG. 4. Dependence of $2nk/\lambda$ on ω for single-crystal zince: 1—without allowance for oxidation; 2—with allowance for oxidation; 3—contribution of free electrons according to [4].

TABLE II. Oscillator strength of interband transitions in zinc

	From experimental data		With allowance for oxidation	
	n_1	n_2	n_1	n_2
From dispersion of ϵ_1	0.79	0.05	0.76	0.08
From absorption	0.61	0.04	0.75	0.05

weaker absorption, especially in the region of the low-temperature maximum, in comparison with the calculations of[6]. There is also a weaker peak near $\lambda = 1.9\ \mu$, which agrees with the predictions of Motulevich and Shubin[4]. In accordance with Stark and Falicov[5] and Kosowski[6], this peak should be identified with the $P_1 - P_2$ transition near the K point of the Brillouin zone, which is allowed if $\mathbf{E} \perp \mathbf{c}$.

It is well known[13] that at $\omega^2 \gg \omega_i^2$, where ω_i is the natural frequency of the optical transition, the electrons participating in the transition behave like free electrons. This means that on the short-wave slope of the absorption band the function $\epsilon_1(\lambda^2)$ is linear, and its slope is determined by the total number N of the electrons participating in the optical phenomena at $\omega < \omega_i$. This enables us to estimate the oscillator strength of the observed interband transitions. Analyzing the linear sections in Fig. 3 and assuming throughout that the mass is equal to the mass of the free electrodes, we obtain for the long-wave section $N_2 = 0.56$ electron/atom and for the short-wave section $N_1 = 1.35$ electron/atom. No significant interband-absorption bands were observed in[4] in the more remote infrared region of the spectrum, and the free-carrier concentration N_0 was found to be 0.51 electron/atom. Judging from the small anisotropy of the static conductivity, and also from the preliminary data of Lenham and Treherne[14], the optical anisotropy of zinc in the infrared region is low; this enables us to consider our results jointly with those of Motulevich and Shubin[7]. Then the differences $n_1 = N_1 - N_2$ and $n_2 = N_2 - N_0$ give the oscillator strengths for both bands (in electron/atom units)—Table II.

The oscillator strengths can be obtained also from the area bounded by the $2nk/\lambda(\omega)$ curve. We have performed the appropriate calculations, after first separating the contributions of the different absorption mechanisms, as shown in Fig. 4, and after extrapolating the curve into the high-frequency region in accordance with the results of Mosteller and Wooten[15]. The oscillator strengths obtained from the absorption data are also given in Table II. The accuracy of the values listed in this table is 0.01, so that a discrepancy by almost 0.2 in the values of n_1 calls for an explanation.

We have assumed that the difference between the oscillator strength determined from two independent characteristics of the metal can be connected with the distorting influence exerted on its optical constants by the thin oxide layer. Assuming that the influence of the oxide can be accounted for by Hall's approximate formulas[16] and that the samples are coated with a zinc oxide layer of thickness 20 Å, we have obtained the characteristics (Figs. 3 and 4) corresponding to the non-oxidized zinc surface. The calculation technique is described in[17]. We see that oxidation greatly distorts the value of the absorption (especially in the short-wave part of the spectrum), but has little effect on the slopes of the linear sections of the $\epsilon_1(\lambda^2)$ curve.

The oscillator strengths calculated from the corrected characteristics are given in the second half of Table II. These data show that the values of n_1 determined by the two methods can be reconciled by making the reasonable assumption that the samples are coated with a layer of oxide. Since the influence of the oxidation on the value of N_0 obtained in[4] could not be taken into account, the discrepancies in the values of n_2 have increased.

The intercept ϵ_0 obtained by extrapolating the linear section of $\epsilon_1(\lambda^2)$ to zero is negative, and the slope of this section determines the quantity $N_1 < 2$. These two circumstances indicate that the interband transitions make an appreciable contribution to the optical characteristics at high frequencies; the total oscillator strength of these transitions is ~0.65 electron/atom.

Rubloff[3] believes that the decrease of R which he observed in the visible and ultraviolet regions of the spectrum at low temperatures agrees with the theoretical predictions of[6]. According to Kosowski[6], when the temperature is raised the third and fourth energy bands at the point L can drop below the Fermi level, so that the transitions from the low-lying bands into these states become impossible. This should lead to a narrowing, from the high-frequency side, of the absorption band that is produced in transitions in the HL direction. However, the question of how this narrowing influences the reflection coefficient calls for a more detailed discussion.

The interband absorption band observed against the background of considerable absorption (strong reflection) by free electrons leads to a lowering of R. In this case, indeed, the increase of the interband absorption in the ultraviolet region following a lowering of the temperature can cause a decrease in the reflection. As seen from Fig. 3, however, the interband absorption in zinc is concentrated in the main at $\omega > \omega_0$, where ω_0 is the frequency at which ϵ_1 for the free electrons vanishes; it is connected with the plasma frequency ω_p by the relation $\omega_0 = \omega_p/(\epsilon_1^{qu})^{1/2}$ (ϵ_1^{qu} is the contribution made to ϵ_1 by the interband transitions). At $\omega > \omega_0$ the free electrons encounter a transparency region with a low reflection coefficient. In this case, the contribution of the free carriers can be neglected completely in a qualitative analysis of interband absorption. Then the enhancement and broadening of the interband-absorption band in the ultraviolet region should lead to an increase of the corresponding reflection maximum and to a shift of this maximum towards higher frequencies, as is indeed observed in our experiments. An indication that the values of R obtained in[3] at T = 77°K are too low was given by Rubloff himself, while the conclusion that these results are in qualitative agreement with theory is based on misunderstanding.

The appreciable increase of reflection at T = 90°K, on the long-wave side of the minimum, indicates that the second absorption band is highly sensitive to temperature. This is not surprising if it is recognized that the Fermi level at the point K passes very close to the extrema of different branches of the energy spectrum, and that the band structure near the point K is very complicated.

---

[1] A. H. Lettington, Proc. of the Intern. Coll. on Optical Prop. and Electronic Structure of Metals and Alloys, Paris, 1965, ed. F. Abelès, North-Holland Publishing Comp., Amsterdam, 1966, p. 147.

[2] R. H. W. Graves and A. P. Lenham, J. Opt. Soc. Am. **58**, 126, 1968.

[3] G. W. Rubloff, Phys. Rev. **B3**, 285, 1971.

[4] G. P. Motulevich and A. A. Shubin, Zh. Eksp. Teor. Fiz. **56**, 45 (1969) [Sov. Phys.-JETP **29**, 24 (1969)].

[5] F. W. Stark and L. M. Falikov, Phys. Rev. Lett. **19**, 795, 1967.

[6] R. V. Kosowski, Phys. Rev. **187**, 885, 1969.

[7] J. P. Beattie, Phil. Mag. **46**, 235, 1955.

[8] I. Yu. Rapp and R. G. Yarovaya, Opt. spektr. **27**, 855 (1969).

[9] L. A. Ageev and I. N. Shklyarevskiĭ, Zh. Prikl. Spektr. **16**, 376 (1972).

[10] R. G. Yarovaya and L. I. Timchenko, Fiz. Tverd. Tela **10**, 1237 (1968) [Sov. Phys.-Solid State **10**, 983 (1968)].

[11] G. Joos and A. Klopfer, Zs. Phys. **138**, 251, 1954.

[12] V. G. Padalka and I. N. Shklyarevskiĭ, Opt. spektr. **11**, 527 (1961).

[13] L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, 1957 [Pergamon, 1959].

[14] A. P. Lenham and D. M. Treherne, J. Opt. Soc. Am. **56**, 752, 1966.

[15] L. P. Mosteller and F. Wooten, Phys. Rev. **171**, 743, 1968.

[16] A. C. Hall, Appl. Phys. **6**, 37, 1965.

[17] V. G. Padalka and I. N. Shklyarevskiĭ, Opt. spektr. **12**, 291 (1962).

Translated by J. G. Adashko
69