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Optical properties of solid Na and Li between 0.6 and 3.8 eV[†]

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Optical constants of Na and Li in the form of evaporated thick solid films have been determined between 0.6 and 3.8 eV by ellipsometry. Measurements were made at room temperature through the quartz substrate at the quartz-metal interface. The optical conductivity of Na agrees well with the earlier data of Smith, while that of Li exhibits considerable differences from the results of Mathewson and Myers. The parameters of the nearly-free-electron model have been derived from the real part of the dielectric function, and the results compared with previous data.

INTRODUCTION

The optical properties of solid alkali metals have been of considerable interest for many years. In the region from the infrared to the near ultraviolet, where the intra- and interband transitions and the plasma frequencies are located, several experimental studies have been reported in the literature, while in the vacuum ultraviolet the optical constants have been determined recently in our laboratory. The optical spectra below their plasma energies have been shown by Mathewson and Myers[1] for Li and Smith[2,3] for the heavier alkali metals to be consistent qualitatively with the predictions of a simple nearly-free-electron model. However, due to severe experimental difficulties in this spectral region, considerable differences are found among the experimental results so far published. Recent studies by Palmer and Schnatterly[4] on Na and K and by Monin and Boutry[5] on Na, K, Rb, and Cs did not confirm any of the earlier results except those for Cs. We have, therefore, reinvestigated the optical properties of solid Na and Li in the region from 0.6 and 3.8 eV, as part of a project to study the optical properties of liquid alkali metals.

SUMMARY OF PREVIOUS WORK

The serious discrepancies occurring in the previous experimental results can be seen most clearly by examination of the optical conductivity σ defined by $\sigma = \omega\epsilon_2/4\pi$, where ϵ_2 is the imaginary part of the dielectric function and ω is the angular frequency of the incident photons. Most of the previous results in the infrared to near ultraviolet on [2,4–9] Na and[1,10,11] Li at room temperature are summarized in Figs. 1 and 2, respectively, as plots of σ versus incident photon energy $\hbar\omega$.

Among the numerous data on Na shown in Fig. 1, only Smith's results[2] may be interpreted simply as a composite of the intraband absorption tail and the interband absorption starting at around 2 eV. The minimum at 1.9 eV in his data has been identified as the threshold for the interband transition, and the position of both the minimum and the maximum at around 2.8 eV have been found to be in good agreement with the predictions of the Wilson-Butcher theory[12] on the free-electron interband transition and of the band-structure calculations based on a single-electron picture.[13] It is well known, on the other hand, that the double peak structure found in Mayer and Hietel's data[9] on Na cannot be explained by such simple theories, and this has stimulated a number of theoretical studies[14–18] on elementary processes of electronic excitations in alkali metals.

In the case of Li, the only data available over the region from the infrared to the ultraviolet are those of Mathewson and Myers.[1] They reported the results as shown in Fig. 2. Curve A was measured for a Li film on a quartz substrate twelve hours after deposition and curve B was measured for the same film seven days after deposition. Curve C was obtained for a Li film on a sapphire substrate. In contrast to the case of Na, the interband thresholds identified from the positions of the minima in these conductivity curves are con-

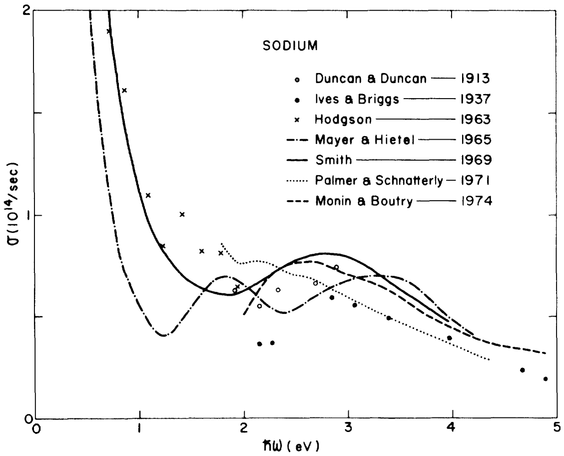

FIG. 1. Optical conductivity vs incident photon energy of solid Na at room temperature.

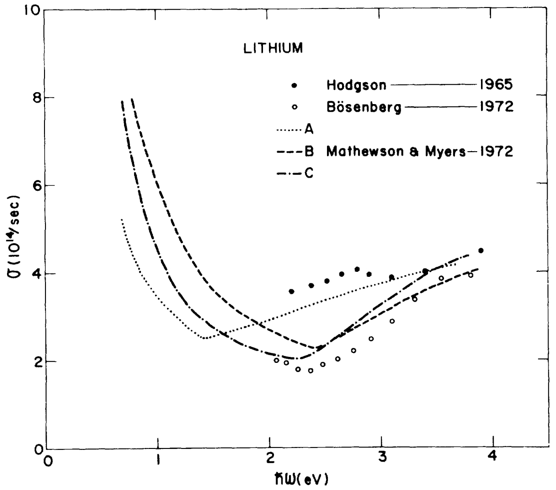

FIG. 2. Optical conductivity vs incident photon energy of solid Li at room temperature.

siderably shifted to energies lower than are predicted by simple theories. The minima in the curves A, B, and C are found at approximately 1.4, 2.3, and 2.2 eV, respectively, whereas the threshold energy expected from the band-structure and free-electron calculations is ~3.0 eV.[19]

The other data presented in Figs. 1 and 2 were taken over very limited spectral regions, and cannot be used to determine the interband thresholds. It should be noted, however, that even if we exclude the earliest data taken before ultrahigh vacuum techniques became available, the differences found in the remaining data are quite significant.[20] The major part of these discrepancies may be attributed to properties of the metal surfaces measured, such as roughness, crystallinity, granularity, and contamination, which in turn depend on the procedures used in the film preparation. Interpretation of the σ-vs-$\hbar\omega$ curves in Figs. 1 and 2 would, therefore, require careful characterization of the metal surfaces in each case. Even for a given metal film, differences in its apparent optical properties have been found when these have been calculated from reflectance measurements at the vacuum-metal interface and at the substrate-metal interface. Such studies have been carried out by Palmer and Schnatterly[4] for Na and by Callcott and Arakawa[21] for Li. Most of the data shown in Figs. 1 and 2, e.g., Duncan and Duncan,[6] Hodgson,[8] and Smith's[2] data for Na and Hodgson[10] and Bösenberg's[11] data for Li, were obtained from reflectance measurements at the substrate-metal interface, mainly in order to avoid oxidation problems.

On the other hand, fairly good agreement is found among the experimental results for ϵ_1, the real part of the dielectric function of Na, indicating that this quantity is relatively insensitive to surface properties. In the case of Li, however, appreciable discrepancies are found in the ϵ_1 data. The previous results of ϵ_1 for Na and Li will be summarized later in terms of the parameters of the nearly-free-electron model, i.e., the effective mass of conduction-band electrons, the ion core polarizability and the plasma energy, and compared with the present results.

EXPERIMENTAL

As in most of the previous studies,[21] the basic technique used in this study to determine the optical constants of metal surfaces was that of ellipsometry. The ellipsometer consisted of a sample compartment equipped with an ultrahigh vacuum system and evaporator, and two optical benches. A monochromator, optical chopper, and polarizer were mounted on a fixed optical bench, and an analyzer and detector were mounted on another bench which was rotatable in the plane of incidence. A photomultiplier tube (EMI, type 9502) was used as the detector in the visible and ultraviolet regions, and a PbS photoconductor (Infrared Industries, type B3-SA6) was used in the infrared. These systems were connected to the sample compartment through quartz windows. Both the entrance and exit windows were checked for spurious polarization by measuring ellipsometric parameters for a gold mirror both under vacuum and at one atmosphere with and without the windows.

The alignments of the polarizer and analyzer relative to the plane of incidence were set up *in situ* using the absolute-minimum method of McCrackin *et al.*[22] First, a quartz prism was placed at the center of the sample compartment such that total internal reflection took place on the base at a 70° angle of incidence with an accuracy of ± 5 min. Then the compartment was sealed and pumped down. The polarizer and the analyzer were then rotated in the vicinity of their respective quadrants until the settings for the minimum transmitted intensity were attained. The residual intensity at the minimum setting relative to the light intensity from the polarizer, or the combined leakage of the polarizer and analyzer, was of the order 10^{-6}. Over the entire wavelength region studied, no deviations greater than 1 min were observed in this setting, indicating that this method of alignment was applicable to our elipsometer. As has been analyzed by McCrackin *et al.*,[22] if the light from the polarizer had appreciable ellipticity this setting would change with wavelength depending on the optical constants of the reflecting surface. After depositing a metal sample onto the base surface of the quartz prism, the setting thus obtained showed no change over the entire spectral region. This also showed that our quartz prisms, used as substrates, had no substantial internal strain. Differences in the minimum setting for different zones did not exceed 3 min, and the averaged values were used for measurements.

Na and Li samples evaporated from tantalum tubes onto the prism surface had original purities of 99.5% and 99.9%, respectively. During evaporation, the prism was maintained at room temperature, and the intensity of the s component of the reflected light was monitored at the wavelength where the metal film shows the maximum transmittance, in order to ensure that the evaporated films were effectively infinitely thick. Evaporations were continued for about three times longer than the period required for the monitored intensity to become constant. In most cases the evaporation was completed in ~2 min. The ratio of the final intensity of the s wave to the initial intensity gave the reflectance of the quartz-metal interface for the s wave, since the reflection prior to the evaporation was total. The observed reflectances were always consistent with those calculated from the optical constants of the metal obtained from the ellipsometric parameters measured as described below. Before and after evaporation, the pressure in the sample compartment was in the low 10^{-9}-Torr range.

Among the wide variety of ellipsometric techniques, the intensity method of Conn and Eaton[23] was employed in this study to measure ψ and Δ defined by $\tan\psi = r_p/r_s$ and $\Delta = \Delta_p - \Delta_s$, respectively, where r_p and r_s are the reflectance amplitudes, and Δ_p and Δ_s are the phase changes upon reflection, of the components of the incident photon with the electric vector parallel and perpendicular to the plane of incidence, respectively. In this method, by setting the polarizer at 45°, ψ is determined from the intensity ratio I_p/I_s of the p and s components of reflected light by $\tan\psi = (I_p/I_s)^{1/2}$, and Δ is determined from the axial ratio $(I_{\min}/I_{\max})^{1/2}$ of the ellipse of the reflected light by $\sin\Delta = \sin 2\xi/\sin 2\psi$, where $I_{\min}$ and $I_{\max}$ are the minimum and maximum intensities measured by rotating the analyzer around the axis of the reflected beam and $\tan\xi = (I_{\min}/I_{\max})^{1/2}$. Prior to the evaporation of a metal sample, the ratio I_p/I_s was measured on the quartz-vacuum interface. I_p/I_s should be unity in this case due to total reflection. These data were used to calibrate the anisotropy of the detectors or of any other optical components. Although the observed deviation of I_p/I_s from unity was always less than 0.01, it would be a source of serious error if this correction was not made to the values of I_p/I_s measured for the quartz-metal interfaces. Using a well-stabilized light source and detector system, the intensity changes resulting from 2 min difference in the settings of the polarizer and analyzer could be detected in the measurements of I_p and I_s.

The advantage of this method is its high sensitivity in determining ψ. As has been discussed by Smith,[2] if β is defined by $\psi = \frac{1}{4}\pi - \beta$, β is quite small for a highly reflecting surface for which r_p/r_s is very close to unity. In fact, using the conventional extinction method, in which the directly measured quantity is essentially the angle ψ, Smith[2] could not obtain reliable values of ψ from a single reflection at a quartz-Na interface due to the relatively low sensitivity of the extinction method. In contrast, since the intensity ratio I_p/I_s can be written for small values of β as $I_p/I_s = \tan^2\psi \simeq 1 - 4\beta$, the present method is four times more sensitive than the extinction method. This method has even higher sensitivity than the modulation method recently developed by Jasperson and Schnatterly[24] and used by Palmer and Schnatterly[4] in their study on Na and K, in which the quantity measured to determine ψ was $(I_s - I_p)/(I_s + I_p) \simeq 2\beta$. The contrast between the present method and the extinction method can be seen clearly in Fig. 3. The values of β measured by Smith[2] for a single reflection at a quartz-Na interface at an angle of incidence of 75° are plotted using open circles in the lower part of Fig. 3. Since no particular structure was found in these data, he had to make multiple reflection measurements, in which he actually measured the quantities 4β and 7β from four and seven reflections at quartz-Na interfaces. His data for 4β are shown in the upper part of Fig. 3 by open circles and these do exhibit a clear structure. The present data obtained from a single reflection at a 70° angle of incidence, and presented by filled circles in the figure, show a structure similar to that in Smith's 4β data. A technique similar to the present one has been used in Mayer and Hietel's study[9] on Na and in Mathewson and Myers's study[1] on Li.

It has been reported[1,25] that the high chemical reactivity of the alkali metals could cause etching of the substrate surface. In the present study, however, substantial differences have not been found between the results for metal films deposited on a new quartz substrate and for films deposited on an old substrate which had already been used several times.

RESULTS AND DISCUSSION

A. Optical conductivity

The optical conductivities of Na and Li, calculated from the measured ellipsometric parameters,[22] are presented in Figs. 4 and 5, respectively, together with Smith's data[2] on Na and Mathewson and Myers's[1] on Li. These results

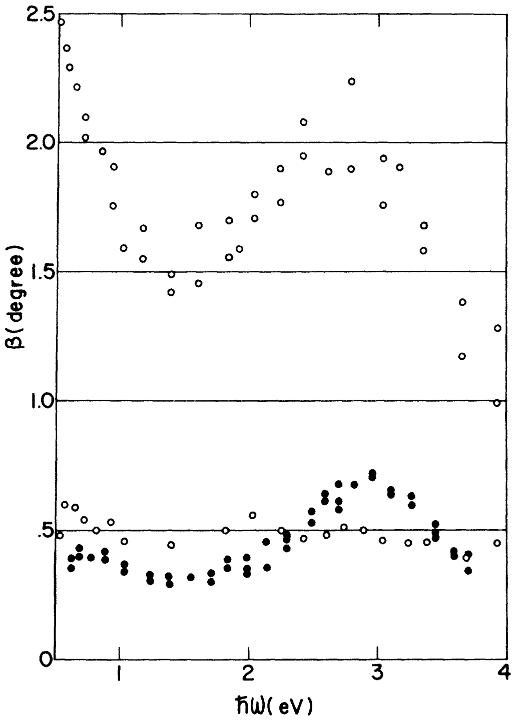

FIG. 3. Values of β defined by $\psi = 45° - \beta$ for a quartz-Na interface. The lower open circles are Smith's data[2] obtained by the extinction method for a single reflection of an incidence angle of 75° and the upper open circles are those for four reflections. The filled circles are the present data by the intensity method for a single reflection at an incidence angle of 70°.

were taken in the period immediately to several days after evaporation. Most of the samples of either metal did not show any appreciable change during this period. A few samples, however, showed considerable changes even one day after evaporation. This will be discussed later. The results for Na shown in Fig. 4 exhibit excellent agreement with those of Smith. The structure starting at about 2 eV is clearly seen in both sets of data. Quantitative agreement in the region of the free-carrier or intraband absorption below 2 eV is almost perfect. The only noticeable difference between our results and those of Smith is that the structure around 3 eV is slightly more pronounced in our data and the peak is shifted to a slightly higher energy. The minimum and the maximum in the present results are at 1.8 and 2.9 eV, respectively, while Smith's results give 1.9 and 2.8 eV. These differences may be attributed to a difference in the degree of crystallinity of the films, since the evaporations of our Na samples were rather rapid as compared with those in Smith's experiments. Thus, Smith's results over the region from the infrared to the near ultraviolet have been confirmed for the first time.

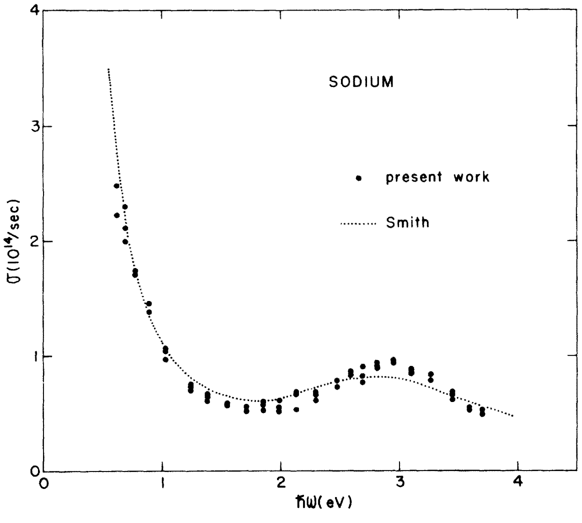

FIG. 4. Optical conductivity of solid Na.

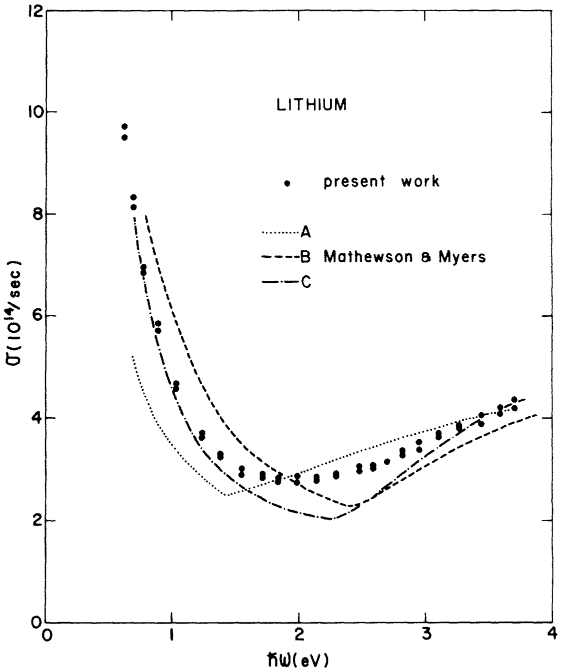

FIG. 5. Optical conductivity of solid Li.

It should be noted, however, that both experiments were carried out under rather similar conditions; in particular, both measurements were made on a quartz-Na interface. Palmer and Schnatterly[4] have made measurements at a vacuum-Na interface in the visible to the near ultraviolet, and have attributed the differences of their data shown in Fig. 1 from Smith's to the presence of the quartz substrate at the reflecting interface in Smith's experiment. The major evidence for this interpretation was that they observed results (not shown in Fig. 1) similar to those of Smith on a glass-Na interface in the visible region. Their results, however, seem to conflict with those of Monin and Boutry[5] which were also taken at a vacuum-Na interface and, as can be seen in Fig. 1, are closer to Smith's results than to Palmer and Schnatterly's.

The results for Li shown in Fig. 5 do not differ very much quantitatively from any of the three curves of Mathewson and Myers, but do show a considerable difference in the shape, especially in the location of the minimum. The position of the minimum in our data is 1.9 eV, while for the curves *A*, *B*, and *C* of Mathewson and Myers it is at 1.4, 2.3, and 2.2 eV, respectively. As previously mentioned, these values deviate significantly from the expected value ~3.0 eV of the theoretical interband threshold, although it is doubtful if we can assign the minimum in the conductivity curve to the interband threshold, because broadening of the absorption edge may shift the apparent onset of absorption.

The present experiment differs from that of Mathewson and Myers in two major points. First in our study the Li films were deposited on the substrates at room temperature, while in their study the films were deposited on substrates cooled by liquid nitrogen. Second, our measurements were made at quartz-Li interfaces, while their measurements were made on vacuum-Li interfaces. They have attributed the differences in their data obtained for the films on quartz (curves A and B) and sapphire (curve C) to the difference of the substrate temperature during evaporation due to their different thermal conductivities, and have assigned curve C to be the most preferable result for Li having a bcc structure. The quite drastic change with time observed for their film on a quartz substrate, i.e., from curve A to curve B, was speculated to be due to a change in crystalline phase[26] of the film, rather than to surface oxidation. If this is correct, the present results may be interpreted as due to a composite of different crystalline structures, because our data over the entire spectral region fall nearly midway between their two curves A and B. As will be shown later, the results for ϵ_1, the real part of the dielectric function, also supports this interpretation.

Contrary to the observations of Mathewson and Myers, most of our films were stable with time. A few of our Li films, however, showed considerable changes with time. A typical example is presented in Fig. 6. The filled circles are the data taken immediately after evaporation and the open circles were taken on the same film one day after evaporation. The results for the fresh film agree well with those of the stable films shown in Fig. 5. In Fig. 6, the appearance of extra absorption at ~2 eV is clear after 1 day. This phenomenon suggests another possible interpretation of the present results on Li. As can be seen in Fig. 5, substantial deviations of our results from curve C of Mathewson and Myers are found only in the region between 1.3 and 3.0 eV. This suggests that this anomalous absorption around 2 eV may occur in all our fresh films to some extent. Unfortunately, any connection between the appearance of this anomaly and the experimental procedures could not be identified definitely. It may be worthwhile to mention, however, that an additional deposition of Li onto the vacuum side of the film after it showed the anomalous absorption did not affect the results in any region of the spectrum. A similar absorption has been observed by Rasigni and Rasigni[25,27] in transmission measurements for Li thin films, and correlated with the granular structures in the films. Although the experimental situation was quite different, this extra absorption just below the interband threshold is similar to those observed by Mayer and Hietel[9] for the surfaces of Na, K, Rb, and Cs in bulk form. A similar anomaly was observed at ~1.5 eV, on a few of our Na films, although it appeared only after several days and to a lesser extent.

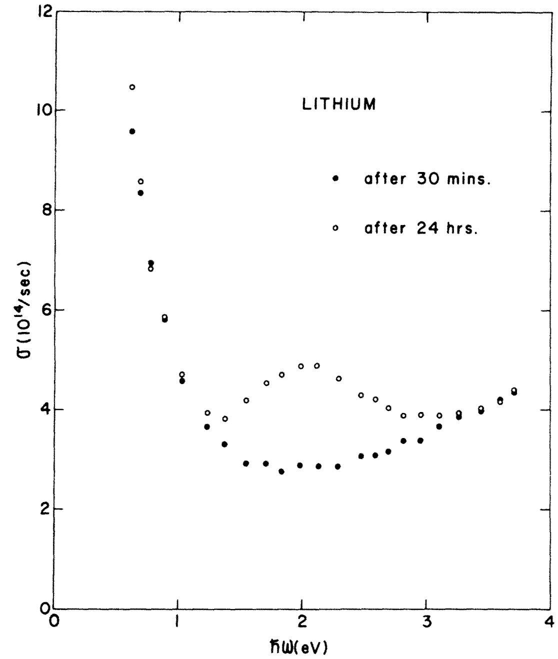

FIG. 6. Optical conductivity of solid Li showing anomalous absorption.

As has been found by Smith[2] and Mathewson and Myers,[1] the experimental values of the optical conductivity of Na and Li below the interband threshold are considerably larger than the Drude

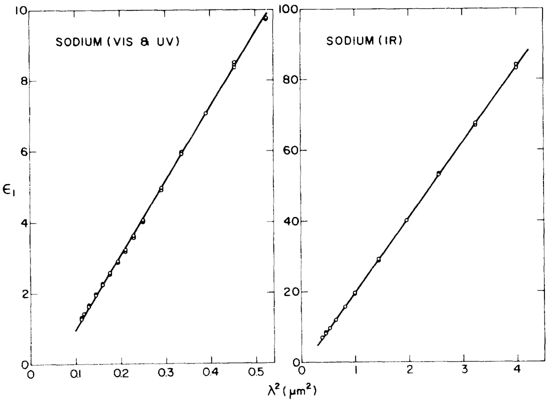

FIG. 7. Real part of the dielectric constant of solid Na.

values[28] given by $\sigma_D = Ne^2/m^*\omega^2\tau$, if σ_D is evaluated from the m^* deduced from the experimental ϵ_1 values and the τ from the dc conductivity, where N is the density of free carriers, m^* is their effective mass, and τ is the relaxation time. The reason for this discrepancy has been discussed by them in terms of excess absorption below the interband threshold and/or broadening of the interband absorption edge. Recent linear-combination-of-atomic-orbitals calculations by Ching and Callaway[13,19] show that the intensity of the interband absorption in Li is larger than that in Na by a factor of 10. The intensities above the threshold energy observed by us do not conflict with this prediction, although the present measurements did not cover the full range of the interband transitions.

B. Real part of dielectric function

The values of ϵ_1 for Na and Li are plotted in Figs. 7 and 8, respectively, as functions of λ^2, the square of the wavelength λ in μm. Fits of the data points to straight lines are quite good. These data have been analyzed in terms of Cohen's expression[29] for ϵ_1,

$$\epsilon_1 = 1 + 4\pi N_0 \alpha - (\omega_a^2/\omega^2) + \delta\epsilon_1 \ , \qquad (1)$$

where N_0 is the atomic density, α is the ion core polarizability, $\omega_a = (4\pi Ne^2/m^*)^{1/2}$, and $\delta\epsilon_1$ is the contribution of the interband transitions to ϵ_1.

TABLE I. Effective electron masses, plasma energies, and polarizabilities of solid Na and Li at room temperature.

	m^*/m (ir)	m^*/m (vis and uv)	m^*/m (vacuum uv)	$\hbar\omega_p$ (eV)	$4\pi N_0\alpha$
Na					
Present work	1.07	1.08	···	5.6	0.1
Ives and Briggs (Refs. 17 and 29)	···	1.01	···	5.64	0.10
Hodgson (Ref. 8)	1.08	···	···	···	···
Mayer and Hietel (Ref. 9)	1.27	1.17	···	···	0.15
Smith (Ref. 2)	1.13	1.07	···	5.65	0.0
Palmer and Schnatterly (Ref. 4)	···	1.00	···	5.4	0.25
Monin and Boutry (Ref. 5)	···	1.07	···	5.61	0.04
Sutherland *et al.* (Ref. 30)	···	···	1.06	5.69	0.03
Li					
present work	1.61	1.56	···	···	···
Hodgson (Ref. 10)	···	1.57	···	···	1.0
Bösenberg (Ref. 11)	···	1.47	···	···	0.8
Mathewson and Myers (Ref. 1)	1.7 (*A*) 1.33 (*B*) 1.33 (*C*)	··· ··· ···	··· ··· ···	··· ··· ···	··· ··· ···
Callcott and Arakawa (Ref. 31)	···	···	1.28 ~ 1.42	6.7	0

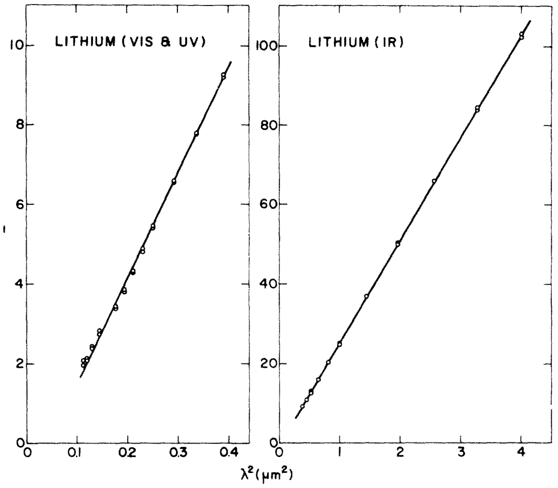

FIG. 8. Real part of the dielectric constant of solid Li.

The only term which makes ϵ_1 vs λ^2 deviate from a straight line is $\delta\epsilon_1$. This term could be evaluated by a Kramers-Kronig relation,[3] if the contribution to ϵ_2 due to the interband transitions were known. Since the present measurements cover only a part of the region associated with the interband transitions, estimates of $\delta\epsilon_1$ have not been made, and the analysis has been made using a simplified version of Eq. (1), i.e.,

$$\epsilon_1 = 1 + 4\pi N_0\alpha - (\omega_a^2/\omega^2) \ . \tag{2}$$

Separate analyses have been performed for m^* using the slopes plotted in Figs. 7 and 8 in the infrared region and in the visible and ultraviolet region, below and above the interband threshold energy, respectively. The plasma energy $\hbar\omega_p$ defined by $\epsilon_1 = 0$ and $4\pi N_0\alpha$ was determined from the intersections of the straight lines with the $\epsilon_1 = 0$ axis and $\lambda^2 = 0$ axis, respectively. The results obtained in this way are compared with previous results in Table I. In the case of Li, however, since the results of $\hbar\omega_p$ and $4\pi N_0\alpha$ do not seem to be meaningful due to the large contribution from the interband transition in the extrapolated region, only the results for m^* are given in the table. Also presented in Table I are the results deduced from data in the vacuum ultraviolet region obtained by Sutherland *et al.*[30] on Na and by Callcott and Arakawa on Li.[31] The present results for Na show reasonable agreement with previous results except for those of Palmer and Schnatterly[4] and of Mayer and Hietel.[9] The results for m^* of Li, on the other hand, exhibit some differences from the previous results.[32] As has been mentioned previously, the present value of m^* for Li in the infrared is intermediate between those reported by Mathewson and Myers corresponding to the conductivity data of curves A and B, indicating that our Li films were possibly intermediate in structure between their films A and B. Variations in the experimental values of m^* of Li suggest a variability of atomic density and, hence, of

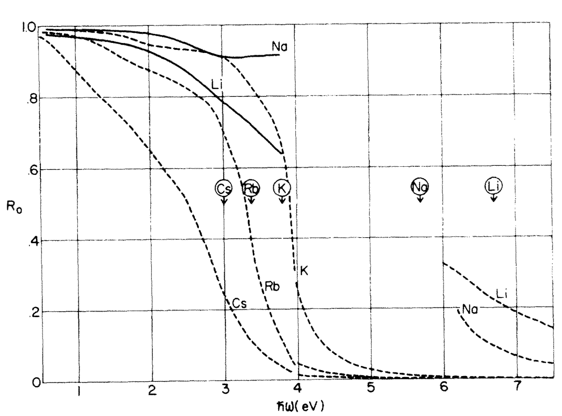

FIG. 9. Normal incidence reflectance of solid alkali metals.

TABLE II. Optical constants of solid Na and Li at room temperature.

	Na		Li	
$\hbar\omega$ (eV)	n	k	n	k
0.6	0.198	9.46	0.663	10.5
0.7	0.146	8.09	0.530	8.99
0.8	0.117	7.02	0.436	7.87
0.9	0.0949	6.24	0.371	6.98
1.0	0.0787	5.59	0.319	6.28
1.1	0.0660	5.05	0.278	5.70
1.2	0.0574	4.62	0.251	5.20
1.3	0.0515	4.23	0.229	4.81
1.4	0.0480	3.87	0.216	4.43
1.5	0.0447	3.64	0.204	4.14
1.6	0.0424	3.40	0.197	3.88
1.7	0.0418	3.15	0.194	3.62
1.8	0.0418	2.96	0.191	3.42
1.9	0.0424	2.78	0.190	3.22
2.0	0.0442	2.62	0.191	3.04
2.1	0.0464	2.48	0.194	2.86
2.2	0.0495	2.36	0.199	2.69
2.3	0.0539	2.23	0.202	2.58
2.4	0.0587	2.10	0.209	2.43
2.5	0.0640	1.99	0.214	2.33
2.6	0.0689	1.88	0.225	2.19
2.7	0.0745	1.80	0.235	2.08
2.8	0.0791	1.71	0.244	1.99
2.9	0.0815	1.64	0.255	1.90
3.0	0.0812	1.56	0.263	1.84
3.1	0.0794	1.50	0.273	1.78
3.2	0.0742	1.44	0.281	1.72
3.3	0.0689	1.38	0.292	1.66
3.4	0.0628	1.32	0.301	1.61
3.5	0.0583	1.25	0.311	1.55
3.6	0.0539	1.19	0.320	1.50
3.7	0.0495	1.14	0.329	1.45
3.8	0.0464	1.08	0.338	1.40

crystalline phase in the solid films prepared by vapor deposition with different temperatures of the substrate.

It is known that ϵ_1 is quite sensitive to the angle of incidence in ellipsometric measurements. The numerical data for ϵ_1 of Li reported by Mathewson and Myers[33] show an apparent break in the straight line at around 1.1 μm in the λ^2 plot. This may be due to an error in the angle of incidence, because there exists no structure in their conductivity data corresponding to this break and they[1,34] report a change in the angle of incidence at around this wavelength from 85° to 75°. The slopes of their straight lines above and below this wavelength gave $m^* = 1.30m$ and $1.50m$, respectively. This should be compared with the error in m^* of about $\pm 0.02m$ due to ± 5 min uncertainty in the angle of incidence in the present study, where m is the electron mass.

The most probable values of the optical constants n and k, the real and imaginary parts of the refractive index, are tabulated in Table II. Using these values, the normal incidence reflectances $R_0 = [(n-1)^2 + k^2]/[(n+1)^2 + k^2]$ were computed, and the results are plotted in Fig. 9 as functions of incident photon energy. Also shown in Fig. 9 are the results of Smith[2,3] on K, Rb, and Cs in the infrared to the near ultraviolet region and the results on a series of five alkali metals in the vacuum ultraviolet measured in our laboratory.[30,31,35–37] In the region between 4 and 6 eV, no experimental data on Na are available. Although Callcott and Arakawa[31] carried out measurements on Li from 3 to 11 eV, they could not determine reliable values for the optical constants in the region below 6 eV with their experimental technique. The arrows shown in the figure indicate the plasma energies defined by $\epsilon_1 = 0$. Those of K, Rb, and Cs were taken from Smith's data[2,3] and those of Li and Na were taken from Callcott and Arakawa's data[31] and Sutherland *et al.*'s data,[30] respectively. The two reflectance curves for Li in the low- and high-energy regions exhibit reasonable agreement with each other, and it appears that they could be connected by a smooth curve. However, studies in the intermediate region would be important, since a strong interband transition is expected for Li in this region. The reflectance for Na is expected to change sharply in the vicinity of the plasma energy, as observed on photographic film by Wood.[38]

CONCLUSIONS

Smith's results on the optical properties of solid sodium have been confirmed for the first time. For solid sodium the locations of the threshold and the first maximum in the absorption spectrum are consistent with simple theories based on the nearly-free-electron model. Solid lithium is more difficult to work with than sodium. Our results for solid lithium show significant differences from the earlier results of Mathewson and Myers, possibly due to differences in the crystalline phases of the films used in the two studies. For solid lithium the locations of the thresholds observed are not consistent with simple band-structure calculations in either study.

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