the $x$ axis in quartz, there still remains a rather large discrepancy in the magnitudes of the theoretical and experimental attenuations.

We have found steps in the attenuation as a function of temperature in quartz specimens containing various degrees of imprefection. These steps are consistent with attenuation peaks at 16±3°K and 24±3°K superimposed on the phonon-phonon attenuation found in perfect specimens. There is a possible correlation between the iron content of the imperfect specimens and the intensity of the peaks. The origin of the attenuation peaks is probably a structural relaxation mechanism or an ultrasonic-phonon–optical-phonon interaction.

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# Optical Constants of TlCl and TlBr with a Comparison of the Kramers-Kronig and "Two-Angle" Methods of Data Analysis*

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The optical constants of TlCl and TlBr were determined in the region of 3 to 21 eV from reflectivity measurements. The low-energy measurements confirm the previous work of Zinngrebe. The high-energy structure is consistent with the available information on relative positions of atomic energy levels and with a plasma resonance associated with approximately 8 electrons per molecule. Both the "two-angle" and Kramers-Kronig methods were used in analyzing the data. The assumption of unpolarized radiation for a near-normal incidence monochromator can cause a considerable error in the results. The "two-angle" analysis is more sensitive to this error than the Kramers-Kronig technique, especially in the region of large values of $n$ and $k$. When polarization effects are not important, the "two-angle" method gives results as good as or better than the Kramers-Kronig analysis.

## I. INTRODUCTION

THE thallium halides, usually classified as ionic materials, have a much larger dielectric constant than most other ionic crystals, and therefore have a similarity to some of the covalent semiconductors. The optical properties of the alkali halides,[1] ionic crystals with low dielectric constants, and semiconductors[2,3] with high dielectric constants have been extensively investigated in the vacuum ultraviolet where the absorption constant for these materials is high. The interpretation of the experimental results for semiconductors has been aided by the large number of theoretical calculations on these materials. For the ionic materials, however, the calculations are not as complete.

The most extensive investigation to date on the optical properties of the thallium halides in the region of high-absorption constant has been an investigation by Zinngrebe[4] on the absorption spectra in the energy range of 3.0–6.7 eV of thin evaporated films of TlCl and TlBr. The temperature dependence of the absorption edge of TlCl at 3.48 eV has been measured by Zinngrebe, and also by Tutihasi.[5] Both investigations seem to indicate that the absorption edge consists of a band edge for fundamental absorption underlying an exciton peak. The first three members of the hydrogenic exciton series of TlBr have been observed in transmission measurements on thin single crystals by Lefkowitz.[6]

The present investigation was undertaken to experimentally evaluate and compare the "two-angle" and Kramers-Kronig techniques for generating the optical constants from reflectivity data and to extend the measurements on TlCl and TlBr through the region of the plasma resonance.

## II. EXPERIMENTAL

A 1-m, 9°-included-angle vacuum ultraviolet monochromator similar to the one described by Johnson[7] was constructed for this investigation. The grating was a Bausch and Lomb 600-lines/mm tripartite replica grating blazed at 1500 Å in first order and overcoated with a 250 Å layer of $MgF_2$. For the experiments

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* Initial part of the investigation was supported in part by a grant from the National Science Foundation.

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[2] M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

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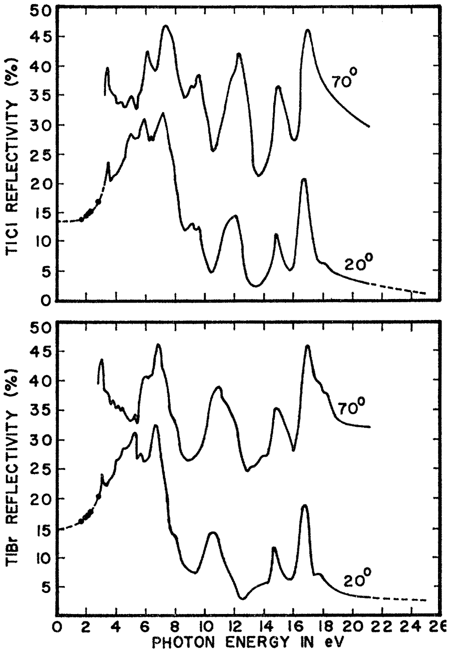

FIG. 1. Reflectivity of TlCl and TlBr at 20° and 70° angles of incidence.

described in this paper, the resolution of the instrument was limited by the size of the geometrical image of the entrance slit at the exit slit. The maximum uncertainty in the wavelength during this investigation was 7 Å.

A McPherson Model 630 Hinteregger gas discharge lamp was operated in a dc mode at 350 mA. Both hydrogen and helium were used at a pressure of approximately 3 Torr. The dc mode produced the hydrogen spectrum from 3 to 13.5 eV and the helium resonance line at 21.2 eV. The same lamp was operated using a condensed spark discharge in commercial grade helium at a pressure of 120 Torr to obtain the continuum from 13.5 to 20 eV.

The sample chamber was of a design similar to that of Smith.[8] A bent $\frac{3}{4}$-in.-diam Pyrex light pipe coated with an evaporated layer of aluminum transmitted the fluorescence from a sodium salicylate layer on the entrance face of the light pipe to either an EMI 9514S or 9607S phototube outside the sample chamber. The light pipe was rotated about an axis coincident with the axis of rotation of the sample holder. The incident and reflected light paths were made equal in length by adjusting the reflecting surface of the sample to contain the axis or rotation of the light pipe.

Reflection measurements were made on single-crystal samples of TlCl and TlBr obtained from Harshaw Chemical Company. The samples were annealed for 24 h at 200°C, as suggested by Smakula,[9] and then polished using a mixture of methyl alcohol, tincture of green soap, and Fisher "B" alumina on a cotton cloth. Although the monochromator including the sample chamber was evacuated to $10^{-6}$ Torr prior to the measurement of reflectivity, the partial pressure of the discharge gas was approximately $10^{-2}$ Torr in the sample chamber during the measurement of reflectivity. A liquid-nitrogen cold trap in series with the 4-in. oil diffusion pump of the monochromator pumping system was used to prevent vapors from condensing on the sample. None of the samples showed a measurable change in reflectivity as a function of time.

## III. RESULTS

The reflectivities of TlCl and TlBr were measured at 20° and 70° angles of incidence over the approximate energy interval of 3 to 21 eV. Reflectivities were determined on a point by point basis at intervals of 0.05 eV between 3 eV and 7.7 eV and at 0.1 eV intervals for energies higher than 7.7 eV. Each point represented the average of four to six experimental readings. After measuring the reflectivity over the desired energy interval the entire process was repeated several times to be certain the results were reproducible. The values for the measured reflectivities in the separate runs differed by no more than 1% in the interval 7.7 to 13.5 eV, 3% in the 3.0–7.7-eV interval, and 5% for energies greater than 13.5 eV. The amount of scattered light was estimated using quartz filters and corrections were made whenever necessary. Anomalous contributions to the reflectivity due to luminescence were not observed although they were looked for by (1) observing the

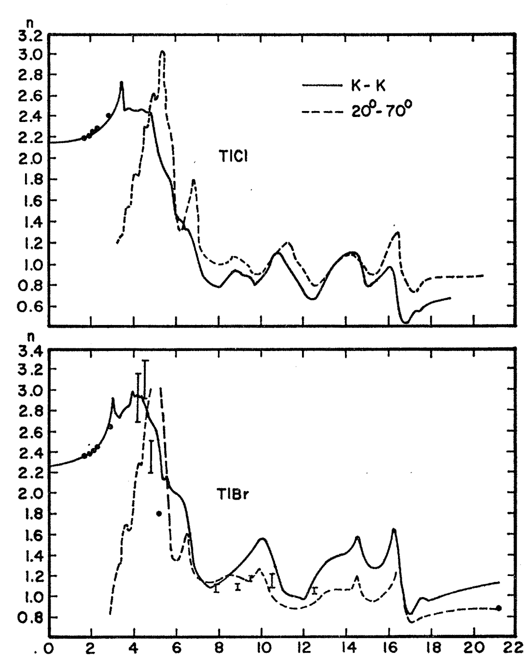

FIG. 2. Index of refraction $n$ of TlCl and TlBr. The points below 3 eV are from the work of Barth (Ref. 11). The values above 3 eV for TlBr represented by points and bars were calculated by the curve-fitting method.

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[9] A. Smakula and M. W. Klein, J. Opt. Soc. Am. **40**, 748 (1950).

reflectivity at high-photon energies without a sodium salicylate phosphor, and (2) placing a quartz plate between the crystal and the sodium salicylate. The curves shown in Fig. 1 are the reflectivities at 20° and 70° angles of incidence for TlCl and TlBr determined from the average of these separate measurements.

Assuming that the radiation from the near normal incidence monochromator is unpolarized, the real and imaginary parts of the complex index of refraction are easily determined from the Fresnel equations using the measured values of the reflectivities at 20° and 70°. For this analysis of the data the family of curves generated as solutions to the Fresnel equations by Ishiguro and Sasaki[10] were used. The real part of the complex index of refraction is referred to in this paper as the refractive index $n$. The variation of $n$ with photon energy calculated by this method is shown by the dashed curves in Fig. 2 for TlCl and TlBr. The absorption index $k$, which is the complex part of the index of refraction, is shown by the dashed curves in Fig. 3 for TlCl and TlBr.

An alternative analysis of the reflectivity data is frequently made by assuming the 20° data to be representative of normal incidence data and then using the Kramers-Kronig dispersion relations to generate $n$ and $k$. As the integrals require the reflectivity over an infinite wavelength interval, some reasonable extrapolations of the measured data are required. For data in the low-energy region the results of Barth's[11] measurements of the index of refraction were used to calculate the reflectivity, and this result was continued to zero energy by use of a French curve. The error due to the infrared approximation was negligible over the region of interest. In the high-energy interval above 21 eV the procedure is more uncertain as data are not available and the extrapolation procedure can result in some error, as will be indicated in the discussion of the results. The function $R(E)=\exp(aE+b)$ was fit to the last two experimental points in the high-energy region of the reflectivity data. For TlCl the values of $a=-0.132$ eV$^{-1}$ and $b=0.7$ were used, while in TlBr $a=-0.1475$ eV$^{-1}$ and $b=-0.145$ were used. The results of the Kramers-Kronig analysis are shown by the solid lines in Figs. 2 and 3. General agreement between the two different analyses of the data exists between 6 and 16 eV. For energies greater than 16 eV, the structure is similar but there is a significant departure between the magnitudes of the results. These magnitudes in this high-energy region are sensitive to the high-energy extrapolation procedure in the Kramers-Kronig analysis. All of the curves show a sharp departure for the two different methods of analysis in the low-energy region. The extremely sharp departure at 5.2 eV of the absorption index for TlBr by the 20°–70° method shown in Fig. 3 suggests that an error exists in these results. Since the polarization of the radiation is the important approximation in the two-angle method, the polarization of the radiation was checked[12] using a LiF pile-of-plates polarizer and the polarization was found to be surprisingly large. The deviations between the two sets of results could be completely explained using the values of the polarization found using the polarizer.

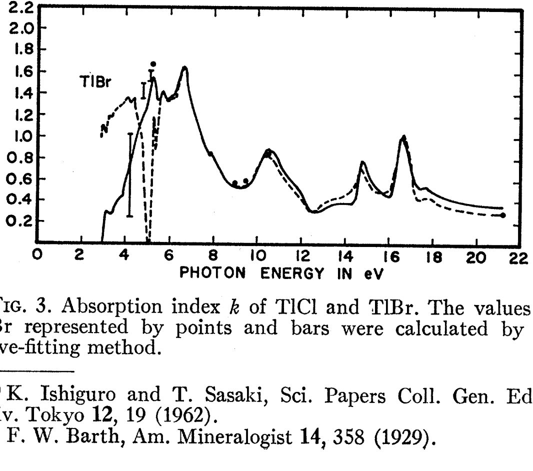

FIG. 3. Absorption index $k$ of TlCl and TlBr. The values for TlBr represented by points and bars were calculated by the curve-fitting method.

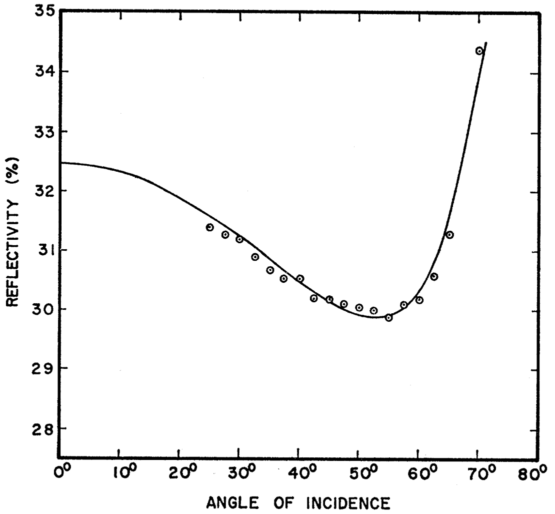

FIG. 4. Reflectivity of TlBr at 5.2 eV as a function of incidence angle. The points are experimental and the curve is the best-fit Fresnel curve for $n=1.80$, $k=1.68$, and $\rho_m=0.60$.

As an independent experimental check on the polarization and the optical constants, the reflectivity was measured as a function of the angle of incidence at several points for TlBr. These results were then fitted by computer with the appropriate Fresnel curve by varying $n$, $k$, and the polarization of the incident light

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[10] K. Ishiguro and T. Sasaki, Sci. Papers Coll. Gen. Educ., Univ. Tokyo 12, 19 (1962).

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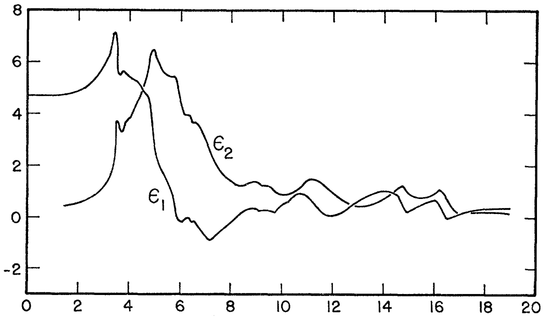

FIG. 5. Real and imaginary parts $\epsilon_1$ and $\epsilon_2$ of the dielectric constant $\epsilon'$ for TlCl.

as parameters. The best-fit curve at 5.2 eV is shown as a solid line in Fig. 4 with the experimental values shown as points. Values of $n$ and $k$ arrived at by this method for 5.2 eV and for other energies are shown as points or vertical lines in Figs. 2 and 3. The length of the vertical lines indicates a range of possible values which would satisfy the experimental results determined by varying the angle of incidence. The results were consistent with the Kramers-Kronig analysis and the values of the polarization calculated using the LiF polarizer.

The results of the Kramers-Kronig analysis differ significantly in amplitude from the results of the other two methods in the high-energy region for TlCl. This difference is caused by the extrapolation into the high-energy region and points out the desirability of using multiple techniques in determining optical constants from reflectivity data.

## IV. OPTICAL PROPERTIES OF TlCl AND TlBr

Since theoretical results are usually presented in terms of the complex dielectric constant, we calculated the real and imaginary parts of the complex dielectric constant $\epsilon'$ as well as the energy-loss function for TlCl and TlBr from the values of $n$ and $k$ determined by means of the Kramers-Kronig analysis of the reflectivity data. The relations between these dielectric constants and the optical constants are

$$\epsilon'=\epsilon_1+i\epsilon_2\,, \tag{1}$$

$$\epsilon_1=n^2-k^2\,, \tag{2}$$

$$\epsilon_2=2nk\,, \tag{3}$$

and

$$-\mathrm{Im}\frac{1}{\epsilon'}=\frac{\epsilon_2}{\epsilon_1^2+\epsilon_2^2}\,. \tag{4}$$

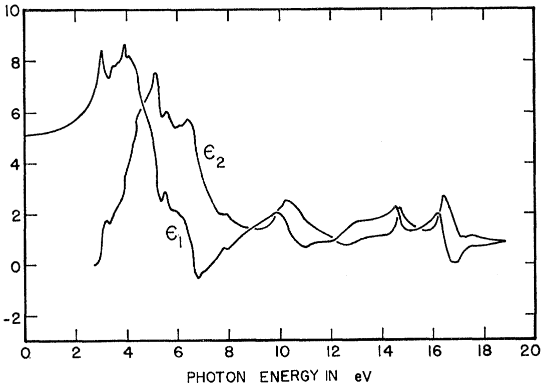

FIG. 6. Real and imaginary parts $\epsilon_1$ and $\epsilon_2$ of the dielectric constant $\epsilon'$ for TlBr.

The values of $\epsilon_1$ and $\epsilon_2$ for TlCl and TlBr as a function of energy are plotted in Figs. 5 and 6. These figures show several peaks in $\epsilon_2$ that can be discussed in terms of particular electron transitions in the materials. (Note that much of the fine structure in the original reflectivity curves has been obscured in the $\epsilon_2$ results. Phillips[13] has shown that the integral transform can obscure the fine structure and also result in a shift of the peaks of about 0.1 to 0.4 eV.)

Previous investigators have associated the steep rise in $\epsilon_2$ at 3.05 eV for TlBr and 3.45 eV for TlCl with the fundamental absorption band edge underlying an exciton peak.[4,5,14] The oscillator-like appearance of the first peak in TlCl at 3.5 eV is consistent with the formation of excitons at this energy. These results cannot be used to ascertain the energy at which band-to-band transitions begin, since the band edge has been assumed to be nearly degenerate with the exciton level and is not resolved from it. The band edge of TlCl has been placed at 3.5 eV by Zinngrebe[4] from the results of his investigation of the temperature dependence of the band edge, and at 3.43 eV by Yanagi[15] because of the sharp rise in the photoconductivity at that energy. Either one of these energies for the band edge would

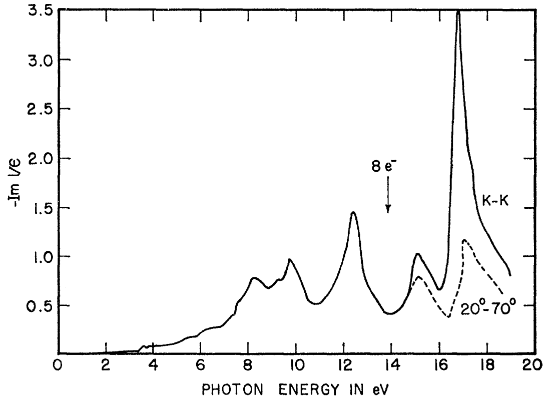

FIG. 7. Energy-loss function $-\mathrm{Im}1/\epsilon'$ for TlCl. The arrow indicates the plasma resonance energy calculated for 8 free electrons per molecule. The solid curve was calculated from the Kramers-Kronig analysis of the data. The dashed curve was calculated above 14 eV using the more reliable high-energy results obtained from the two-angle measurements.

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[14] W. Martienssen, J. Phys. Chem. Solids **8**, 294 (1959).

[15] T. Yanagi, J. Phys. Soc. Japan **18**, 1552 (1963).

not be resolved from the exciton peak in the room-temperature data presented here.

The absorption edge in TlBr is not oscillator-like in appearance, in contrast with TlCl, but exhibits the behavior calculated by Korovin[16] for transitions between parabolic energy bands, in which $\epsilon_2$ does not exhibit a peak and $\epsilon_1$ peaks at an energy corresponding to the band gap. In light of these results, the analysis of the data in Fig. 3 for TlBr places the band gap for the onset of band-to-band transitions at 3.05 eV. The exciton peak observed by Lefkowitz[6] is very weak. Lefkowitz has placed the band edge at 3.115 eV by a calculation of the ionization energy of the excitons observed in his work. This assignment agrees with the assignment of 3.05 eV made above within the uncertainty in the present results.

The peaks in TlCl at 4.95, 5.05, 5.82, and 6.02 eV, and in TlBr at 4.07, 4.48, and 5.06 eV, observed by Zinngrebe[4] and associated by him with excited electronic states of the thallium and halide atoms, are observed in the reflectivity data presented in Fig. 1, but appear only as points of inflection in Figs. 3, 5, and 6 for the absorption index *k* and the imaginary part $\epsilon_2$ of the complex dielectric constant. In addition, the reflectivity and $\epsilon_2$ for TlBr show a peak of 5.6 eV, corresponding to the excited state of both the thallium and bromine atom, which is missing from the absorption data of Zinngrebe shown in Table I. The results of this research are consistent with Zinngrebe's interpretation in the low-energy region.

TABLE I. Low-energy absorption peaks in the thallium halides by Zinngrebe (Ref. 4).

| TlCl (eV) | TlBr (eV) | Interpretation |
|---|---|---|
| 3.46 | 3.04 | Exciton formation and the beginning of band-to-band transitions |
| 4.95 | 4.07 | $Tl^+ + (Cl^-, Br^-) + h\nu \rightarrow Tl + (Cl, Br)$ |
| 5.05 | 4.48 | $\rightarrow Tl + (Cl, Br)^*$ |
| 5.82 | 5.06 | $\rightarrow Tl^* + (Cl, Br)$ |
| 6.02 | (5.48)[a] | $\rightarrow Tl^* + (Cl, Br)^*$ |
| $^2P_{3/2}$-$^2P_{1/2}$ | for Cl = 0.11 eV<br>for Br = 0.45 eV | |
| $^2P_{1/2}$-$^2P_{3/2}$ | for Tl = 0.96 eV | |

[a] Not found in Ref. 4 but present investigation shows structure in reflectivity at this energy.

The remaining peaks cannot be exactly interpreted without the aid of detailed band calculations. However, several observations can be inferred from the present data. The rapid decrease in the reflectivity after 7.2 eV for TlCl and 6.7 eV for TlBr is similar to the behavior of certain metals in the ultraviolet.[15,17] Here the valence electrons are essentially unbound and able to perform collective oscillations. The number of electrons per molecule taking part in these collective oscillations can be calculated from the value of the plasma resonance frequency $\omega_p$ associated with these oscillations. This frequency has long been associated[18] with a single large peak in the energy-loss function for fast electrons traversing the material. This peak has been observed in conventional energy-loss experiments[19] in which inelastically scattered electrons are energy analyzed. The results of energy-loss measurements can also be inferred from optical data.[20] The energy-loss function defined in Eq. (3) is plotted as a function of energy for TlCl and TlBr in Figs. 7 and 8. Since the values of $\epsilon_1$ and $\epsilon_2$ calculated from the Kramers-Kronig analysis are thought to be less accurate than the "two-angle" method beyond 16 eV, the values calculated from graphical analysis are also determined and shown as a dashed line in Fig. 7 for TlCl. Peaks appear in these functions in a one-to-one correspondence with peaks in $\epsilon_2$, though shifted ($\sim$0.3 eV) to slightly higher energy. The low-energy peaks are small, due to the magnitude of $\epsilon_1$ and $\epsilon_2$ in this region. This structure can be associated with interband scattering and is analogous to results obtained for the alkali halides by Phillip and Ehrenreich.[1] In addition to these interband scattering peaks, a large broad peak appears at 11.8 eV for TlBr and at 12.4 eV for TlCl. In each of these materials this

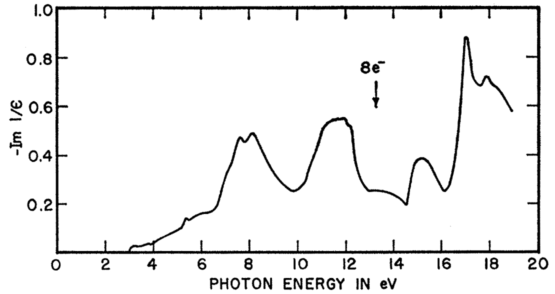

FIG. 8. Energy-loss function $-\mathrm{Im}1/\epsilon'$ for TlBr. The Kramers-Kronig analysis of the data was used. The arrow indicates the plasma resonance energy calculated for 8 free electrons per molecule.

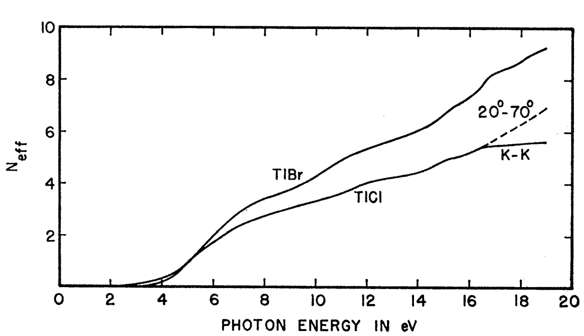

FIG. 9. Effective number of electrons $n_{\mathrm{eff}}$ contributing to the optical properties of TlCl and TlBr as a function of photon energy. For TlCl the integral has also been calculated using the two-angle results and shown as a dashed line while the solid lines are for the Kramers-Kronig analysis.

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[17] H. Ehrenreich and H. R. Philipp, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962).

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[19] C. J. Powell, Proc. Phys. Soc. (London) **76**, 593 (1960).

[20] P. Nozieres and D. Pines, Phys. Rev. **113**, 1254 (1959).

TABLE II. Atomic energy levels for chlorine, bromine, and thallium.[a]

| | Level | Energy (eV) below the continuum | Number of electrons per level in ion |
|---|---|---|---|
| Chlorine | $2s$ | 277 | 2 |
| | $2p$ ($L_{\text{II}}$) | 201.6 | 6 |
| | $2p$ ($L_{\text{III}}$) | 200.0 | |
| | $3s$ | 17.5 | 2 |
| | $3p$ | 6.8 | 6 |
| Bromine | $3p$ ($M_{\text{IV}}$) | 70.1 | 10 |
| | $3p$ ($M_{\text{V}}$) | 69.0 | |
| | $4s$ | 27.3 | 2 |
| | $4p$ ($N_{\text{II}}$) | 5.2 | 6 |
| | $4p$ ($N_{\text{III}}$) | 4.6 | |
| Thallium | $5p$ | 75.4 | 6 |
| | $5d$ ($O_{\text{IV}}$) | 15.3 | 10 |
| | $5d$ ($O_{\text{V}}$) | 13.1 | |
| | $6s$ | $-3.2$ | 2 |

[a] J. A. Bearden and A. F. Burr, U. S. Atomic Energy Commission Report No. NYO-2543-1, 1965 (unpublished).

peak is separated by a much larger energy interval ($\sim$2 eV) than the interband scattering peaks from any of the peaks in $\epsilon_2$. Results for the alkali halides are similar but not as pronounced. In order to locate the plasma resonance peak for the thallium halides, we estimated the density of "free" electrons in the conduction band able to undergo collective oscillations. Using a tabulation of atomic energy levels, an estimate of the energy gaps for TlCl and TlBr was made on the basis of the information shown in Table II. This table indicates that one would expect eight free electrons per molecule at an energy above $\sim$10 eV for both TlBr and TlCl; two electrons from the $\text{Tl}^+$ $6s$ band, and six electrons from the next lower-lying $\text{Br}^-$ $4p$ band or the $\text{Cl}^-$ $3p$ band. The next lower levels, the halide $s$ bands, are $\sim$30 eV below the continuum and would not be expected to contribute to optical processes in this region. The plasma resonance energy $h\omega_p$ is calculated from the expression[20]

$$\tfrac{1}{2}\pi\omega_p{}^2=\int_0^\infty \omega\epsilon_2(\omega)d_\omega=\frac{2\pi^2Ne^2}{m}n. \tag{5}$$

This gives

$$h\omega_p=\left(\frac{4\pi^2Ne^2}{m}n\right)^{1/2}, \tag{6}$$

in which $N$ is the molecular density of the crystal in molecules/cc and $n$ is the number of free electrons per molecule. Using a value of eight electrons per molecule for $n$, the calculated plasma resonance energy is 13.5 eV for TlBr and 13.9 eV for TlCl.

If the assumption is made that the broad peak in the energy-loss function at 11.8 eV for TlBr and 12.4 eV for TlCl consists of a low-energy peak associated with the interband transitions at 10.2 eV for TlBr and 11.2 eV for TlCl, and of a higher-plasma resonance peak unresolved from the interband peak, the calculated values of the plasma resonance energy assuming eight electrons per molecule are in good agreement with the experimental data.

For a finite range of integration, Eq. (7) can be used to define $n_{\text{eff}}$,[1,21] an effective number of free electrons contributing to the optical properties in the range up to a given energy:

$$\left(\frac{2\pi^2Ne^2}{m}\right)n_{\text{eff}}=\int_0^{\omega_0} \omega\epsilon_2(\omega)d_\omega. \tag{7}$$

In the absence of bands lower than the $p$ bands of the halide ion, $n_{\text{eff}}$ would be expected to saturate at a value of 8. A plot of $n_{\text{eff}}$ as a function of energy from a computer calculation using the Kramers-Kronig values of $\epsilon_2$ for TlCl and TlBr are shown in Fig. 9. For TlCl the graphically determined values of $\epsilon_2$ were also used above 14 eV with the results shown as a dashed line. The curves of Fig. 9 indicate that there is considerable contribution from lower-lying electron states to the optical properties of these materials only at a fairly high energy. The fact that $n_{\text{eff}}$ is less than 8 in the region of the plasma resonance indicates that the oscillator strength for valence-band excitation is not exhausted in the region of the plasma resonance.

The last two peaks at 14.7 and 16.4 eV are oscillator-like, and can reasonably be associated with atomic transitions in the $\text{Tl}^+$ ion. The association with the thallium ion is based on the evidence that the peaks appear at exactly the same energy for both TlCl and TlBr.

## ACKNOWLEDGMENTS

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[21] H. R. Philipp and H. Ehrenreich, Phys. Rev. Letters 8, 92 (1962).