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OPTICAL PROPERTIES OF EPITAXIAL
PbS FILMS IN THE ENERGY RANGE 2-6 eV

By

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ABSTRACT

The reflectivity of epitaxial PbS films has been compared with the reflectivity of bulk PbS in the energy range 2.1 to 6.2 eV and found to agree in both magnitude and structure within a few percent at energies where interference effects can be neglected. The transmission of several films with thicknesses varying from 335 Å to 550 Å has been measured and the structure and shape of the spectra shown to be the same for the films with different thicknesses. The reflectivity of bulk PbS between 2.1 and 6.2 eV has been combined with measurements made by other workers outside of this range to compute optical constants from the Kramers Kronig relation. The optical constants obtained in this manner appear to agree quite well with those obtained from the reflectivity and transmission of the films, considering the experimental difficulties experienced in measuring film thickness and the absolute magnitude of the reflectivity.

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I. Introduction.

The high absorption coefficient and the difficulty in preparing very thin crystalline samples has, until recently, made it impossible to use transmission to study the optical properties of semiconducting materials at energies above the fundamental gap. Information on the optical properties above the gap has, thus, had to be obtained from analyses of reflectivity measurements only. Such reflectivity analyses have been made by Avery (.4 to 3.0 eV)¹ and Cardona and Greenaway² (.5 to 25 eV). Transmission data in addition to reflectivity data, can, however, be obtained from thin films grown epitaxially on appropriate transparent substrates. Several workers^{3,4,5,6} have shown that PbS can be grown epitaxially on NaCl substrates. A number of recent papers have reported the use of PbS films to obtain optical data.^{7,8,9,10,11,12} Of specific interest here, the optical constants have been calculated from reflectivity and transmission measurements on epitaxial films in the region .1 to 1.5 eV by Schoolar and Dixon¹¹ and in the region 1 to 5 eV by Wessel.¹² The values obtained differ considerably from those reported by Cardona and Greenaway.²

We have grown epitaxial films of PbS on both NaCl and KCl substrates and compared the reflectivity to that of bulk PbS. We have found agreement to within a few percent at wavelengths where interference is not important.

Our reflectivity measurements, although having an estimated error larger than that claimed by Wessel, indicate, as do Wessel's, that the reflectivity of PbS is higher than that reported by Cardona. We have

calculated n and k from the Kramers Kronig relation using our bulk reflectivity measurements in the energy range 2.1 to 6.2 eV and those of other workers outside this range. The optical constants obtained in this manner agree quite well with optical constants obtained from our reflectivity and transmission measurements and with those of Wessel.

II. Experimental.

A. Sample Preparation.

The PbS films were prepared in a manner similar to that described by Schoolar and Zemel.⁶ Powdered natural PbS was evaporated in a vacuum of about 5×10^{-6} mm Hg from a boron nitride crucible held in a tantalum resistance heater. The temperature of the PbS was measured by a platinum - platinum rhodium thermocouple placed within the boron nitride crucible. The substrate was clipped to a tantalum plate 20 cm above the evaporation crucible and heated by a tantalum wire heater located just above the plate. A thermocouple attached to the tantalum plate was used to monitor the substrate temperature during evaporation. Some evaporations were also made directly from a tantalum boat. We were not able to detect any effect of tantalum contamination on either the film optical properties or electron diffraction patterns.

We used substrates 1 cm x 1 cm x about 3mm. thick, cleaved in air within a few minutes preceding an evaporation run. The films were grown at a substrate temperature of 300°C, the substrate heater being energized for about 45 minutes before beginning the evaporation to insure equilibrium

conditions. For all samples reported here except one on KCl, the source temperature was approximately 750°C which yielded evaporation rates between 40 and 80 Å/minute. The film on KCl (the source temperature was not recorded) was deposited at an evaporation rate of about 200 Å/minute. Our method of film preparation appears to be essentially the same as that of References 5, 6, 11 and 12.

We used electron diffraction to determine the crystalline quality of the films. Figure 1 shows the reflection diffraction pattern for sample 1, the pattern being typical of that of a (100) cubic face. Figure 2 shows the pattern from a much thicker film (>1000 Å) and demonstrates that the pattern is not coming from electrons penetrating the film to and from the substrate. A further demonstration of this latter fact is given by Figure 3, which shows the transmission diffraction pattern of a film removed from the substrate by dissolving the substrate in water. Films grown on KCl were studied by electron reflection diffraction, the patterns being identical to those of Figures 1 and 2.

Approximately 25 films were grown by the method described above on substrates of NaCl, KCl and CaF_2 . At least partial optical analyses were made on approximately 10 of these films. The results reported here for four films appear to be representative of epitaxial PoS films.

B. Optical Measurements.

The optical system is that described by Grant¹³ and is shown in Figure 4. The dotted line shows the path from sample to phototube during

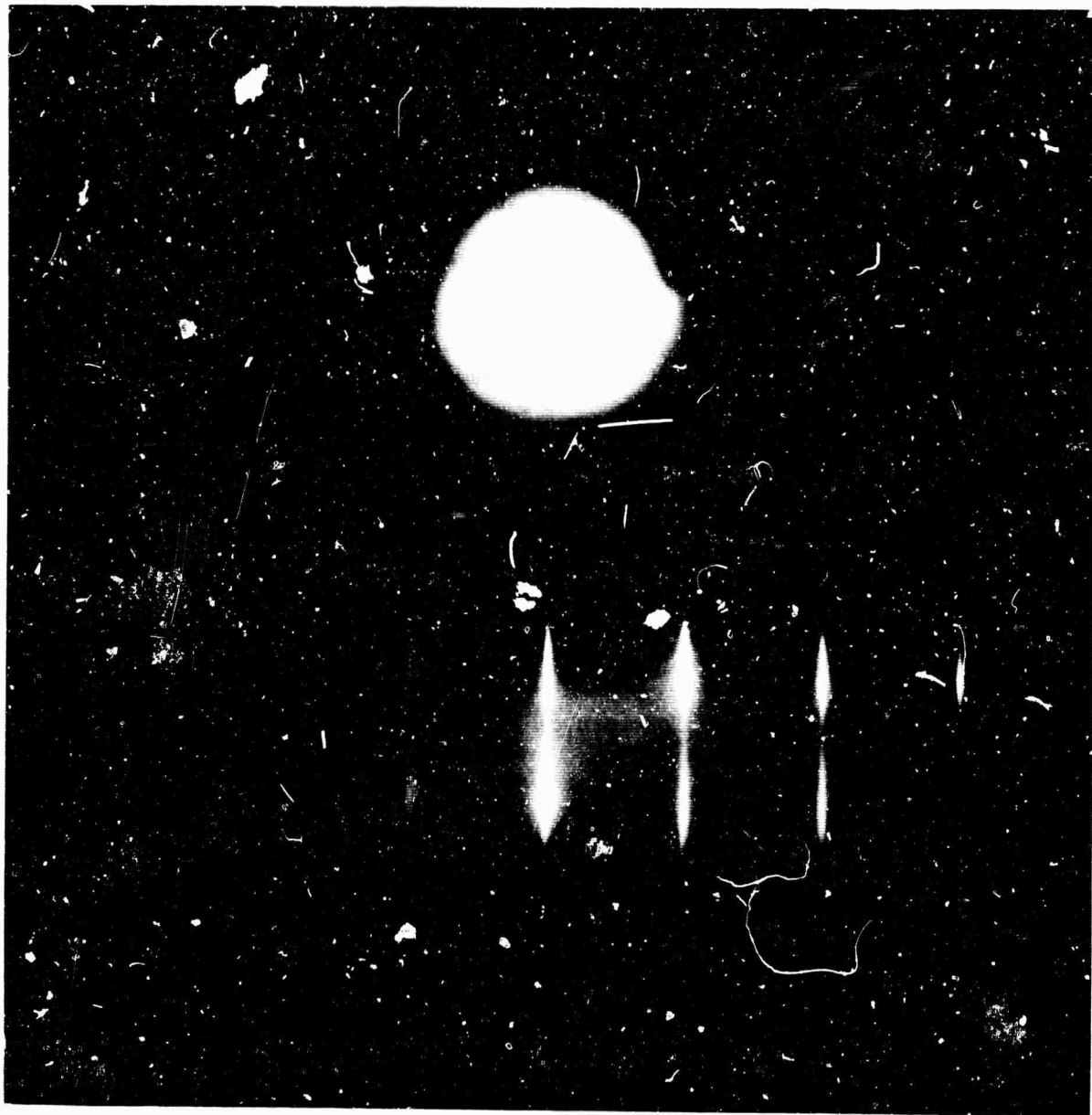


FIG. 1 ELECTRON REFLECTION DIFFRACTION PATTERN OF 335A
FILM (SAMPLE 1).

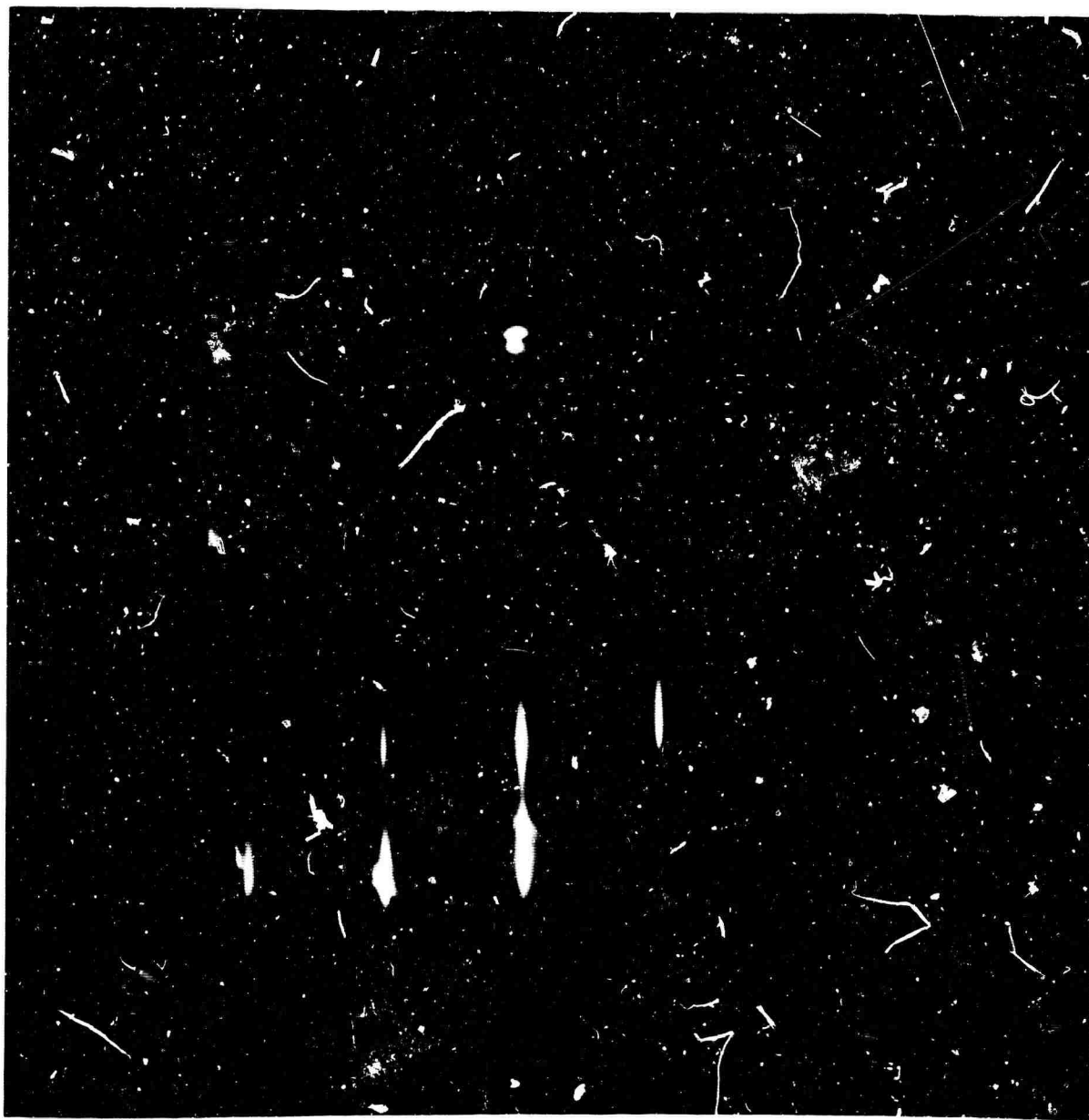


FIG. 2 ELECTRON REFLECTION DIFFRACTION PATTERN OF 1000A.
FILM.

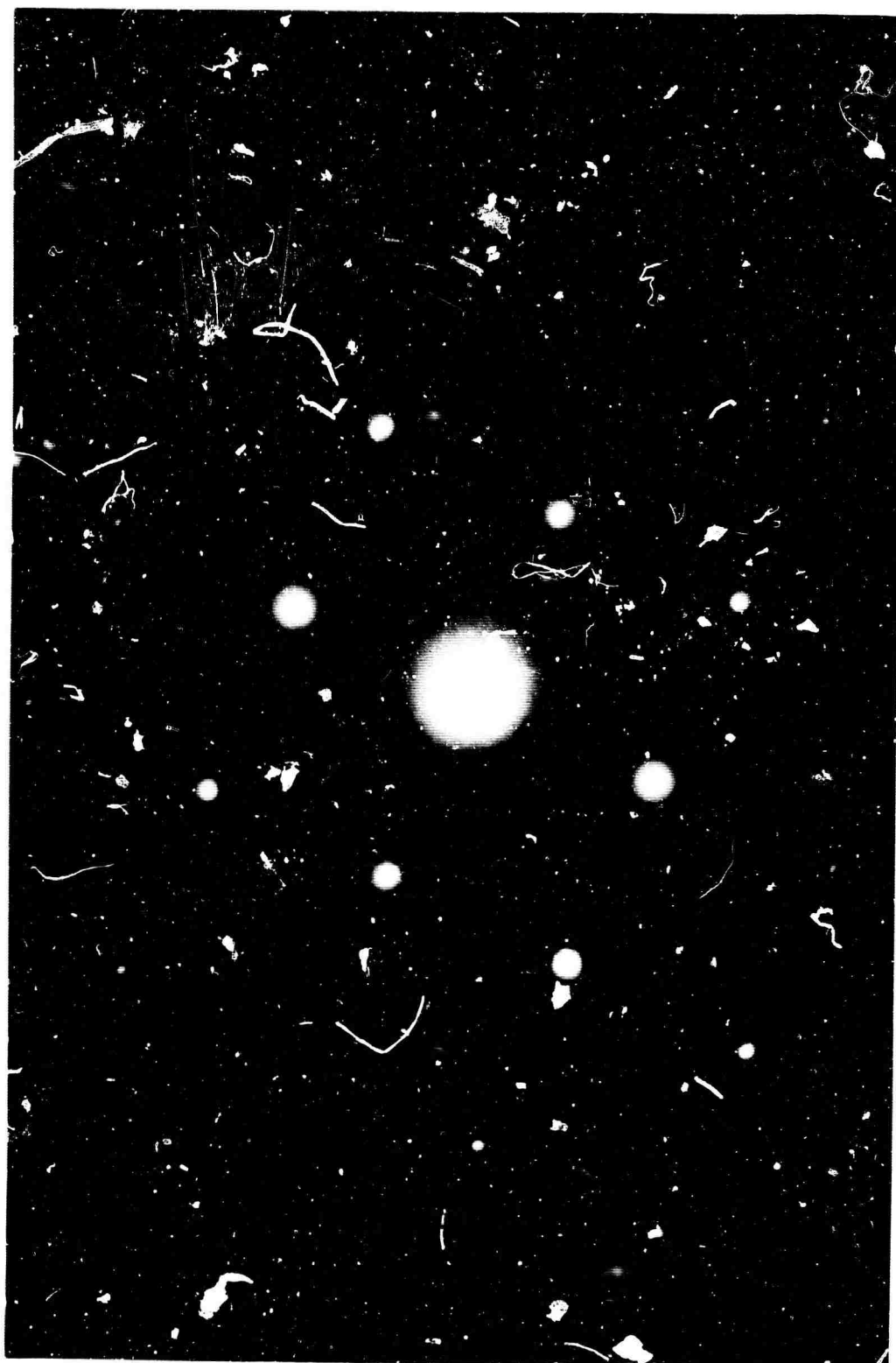


FIG. 3 ELECTRON TRANSMISSION DIFFRACTION PATTERN OF FILM
REMOVED FROM NaCl SUBSTRATE.

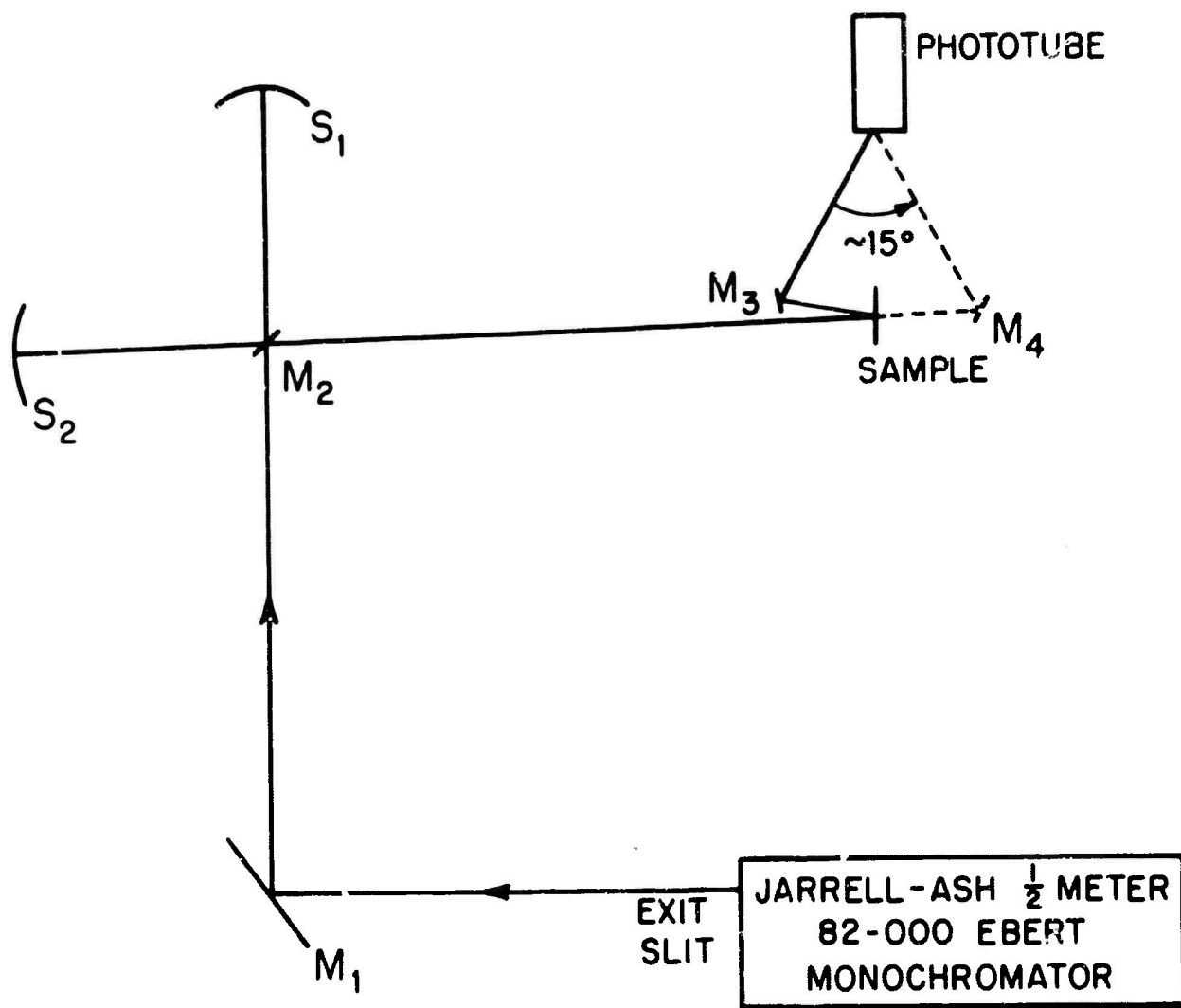


FIG. 4 OPTICAL SYSTEM. S_1 AND S_2 ARE SPHERICAL MIRRORS AND M_1 , M_2 , M_3 , AND M_4 ARE PLANE MIRRORS. THE DOTTED LINE SHOWS THE PATH FROM SAMPLE TO PHOTOTUBE FOR TRANSMISSION AND THE SOLID LINE SHOWS THE PATH FOR REFLECTION.

transmission, and the solid line shows the path during reflection. The beam from the exit slit is focussed on the small plane mirror M_2 by spherical mirror S_1 . Spherical mirror S_2 then focusses the light on either M_3 or M_4 depending upon whether reflection or transmission is to be measured. The beam is nearly in focus at the sample since the distance from the sample to mirrors M_3 and M_4 is small (1.5 cm). The total path length between the sample and phototube is kept small to minimize the effect of any scattering by the sample. The beam strikes mirror M_3 (or M_4) at an angle of about 45° . Provision is made for moving the sample along a line connecting M_3 and M_4 in order that the reflecting surface can be positioned half way between the mirrors. The sample is moved in a vertical plane out of the beam for measuring I_0 and then into the beam for either reflection or transmission, the light to M_4 being blocked during reflectivity measurements and the light to M_3 being blocked during transmission measurements. To insure that they would have identical reflectivities, mirrors M_3 and M_4 were deposited commercially during the same evaporation.

The beam is defocused slightly at the phototube and, thus, the radiation falls on almost the entire sensitive area of the tube cathode minimizing any error in reflectivity measurements due to different regions of the cathode having different sensitivities. The reflectivity of the bulk sample was measured with mirrors M_3 and M_4 in their normal position and with the two mirrors interchanged. It was determined that the mirrors had nearly identical reflectivities. In addition, measurements were taken with the tube rotated

180° about its axis and corrections applied to all reflectivity data to partially account for variations in cathode sensitivity and image intensity as a function of position on the cathode. The corrections applied to the reflectivity as a result of turning the phototube 180° were quite large (of the order of $10^4\%$) and were wavelength dependent. We, thus, consider the major source of error in our reflectivities to be due to variations in phototube sensitivity across the cathode. The reflectivity spectra of all the films and of the bulk sample were measured with the phototube in the same orientation. An identical correction based on turning the tube 180° was then applied to all data. Thus, an error in the reflectivities due to variation in the sensitivity of the cathode with position will affect all data in the same manner and will not affect the agreement in reflectivity between the films and the bulk.

C. Thickness Measurement.

It was originally hoped that a direct measurement of the film thicknesses could be made using the interferometric technique of fringes of equal chromatic order.^{14,15, 16} We expected this method to be accurate to within $\pm 10\%$. We were unable to use the technique, however, because the cleavage planes of the substrates made it impossible to interpret the interference pattern. Therefore, we determined the thicknesses by measuring the transmission at 1, 1.5, and 2 microns and by assuming the optical constants of Schoolar and Dixon.¹¹ Several methods of cross-checking were added. We deposited two films on heated (to $\sim 300^\circ\text{C}$) microscope slides and compared the thickness obtained from the infra-red transmission against a direct measurement using fringes of equal chromatic order. The values agreed within our estimated error in using the fringes of equal chromatic order ($\sim \pm 10\%$). The films on the microscope slides were approximately 450 Å thick.

The transmission of one of the films was found to be nearly identical with that of an epitaxial film at 2, 1.5, 1, .6, and .5 microns. At wavelengths less than 5000 Å the transmission fell somewhat more rapidly than that for an epitaxial film presumably due to scattering by the crystallites in the film. The minimum at 3.5 eV which occurs in the epitaxial films (see Figure 6), however, was quite clearly present.

A small error in the measurement of the infra-red transmission can give quite a large error in the thickness. The cleavage planes in the substrate and/or pinholes in the films caused variations in transmission at different points on the same sample. We, therefore, made our transmission measurements with the beam focussed on what appeared to be the best portion of the sample (minimum pinholes and clearest substrate). We used consistency of results among the samples as well as agreement with the Kramers Kronig values to further insure that we were measuring the infra-red transmission at a point on each sample where pinholes and cleavage planes would have a minimum effect. We consider the thickness values obtained to be accurate to approximately $\pm 15\%$. The largest portion of any error is undoubtedly systematic and will affect all the thickness measurements in the same way.

We had two films on NaCl and one on a glass microscope slide chemically analyzed by a commercial company to determine the total lead content. From this, and a measurement of the film area we hoped to obtain a check on the measurement of thickness by infra-red transmission. The company performing the analysis claimed an accuracy of $\pm 2\%$. The thickness of the films on NaCl determined in this way were considerably smaller ($\sim 30-40\%$) than the

thicknesses obtained by use of the infra-red transmission. The thickness of the film on the glass slide, however, was larger by about 15% than the thickness obtained by infra-red transmission and the thickness obtained from the fringes of equal chromatic order. In view of the inconsistencies in the results of the chemical analyses, we chose to disregard them.

III. Results and Discussion.

A. Reflectivity and Transmission.

Reflectivity and transmission measurements were made on four selected films ranging in thickness, t , from 335 Å to 550 Å (Sample 1, $t = 335$ Å, Sample 2, $t = 410$ Å, Sample 3, $t = 475$ Å, and Sample 4, $t = 550$ Å). Samples 1 through 3 were grown on NaCl substrates and Sample 4 on KCl. In addition, the reflectivity of a cleaved bulk sample was measured. The results are shown in Figures 5 and 6.

The reflectivities agree within about 4% in magnitude (except at low energies where interference effects occur), all samples showing a peak between 3.6 and 3.7 eV and a peak between 5.1 and 5.5 eV in agreement with the results for the energies reported by Cardona and Greenaway.² Our reflectivities are higher than those of Cardona and Greenaway, but agree within a few percent with those of Wessel.¹² The agreement between the film and bulk reflectivity is a measure of the quality and smoothness of the films. The reflectivities were repeatable to within $\pm 3\%$ and we estimate the total error from the optics including alignment, differences in the reflectivities of mirrors M_3 and M_4 and variations in sensitivity across the phototube cathode

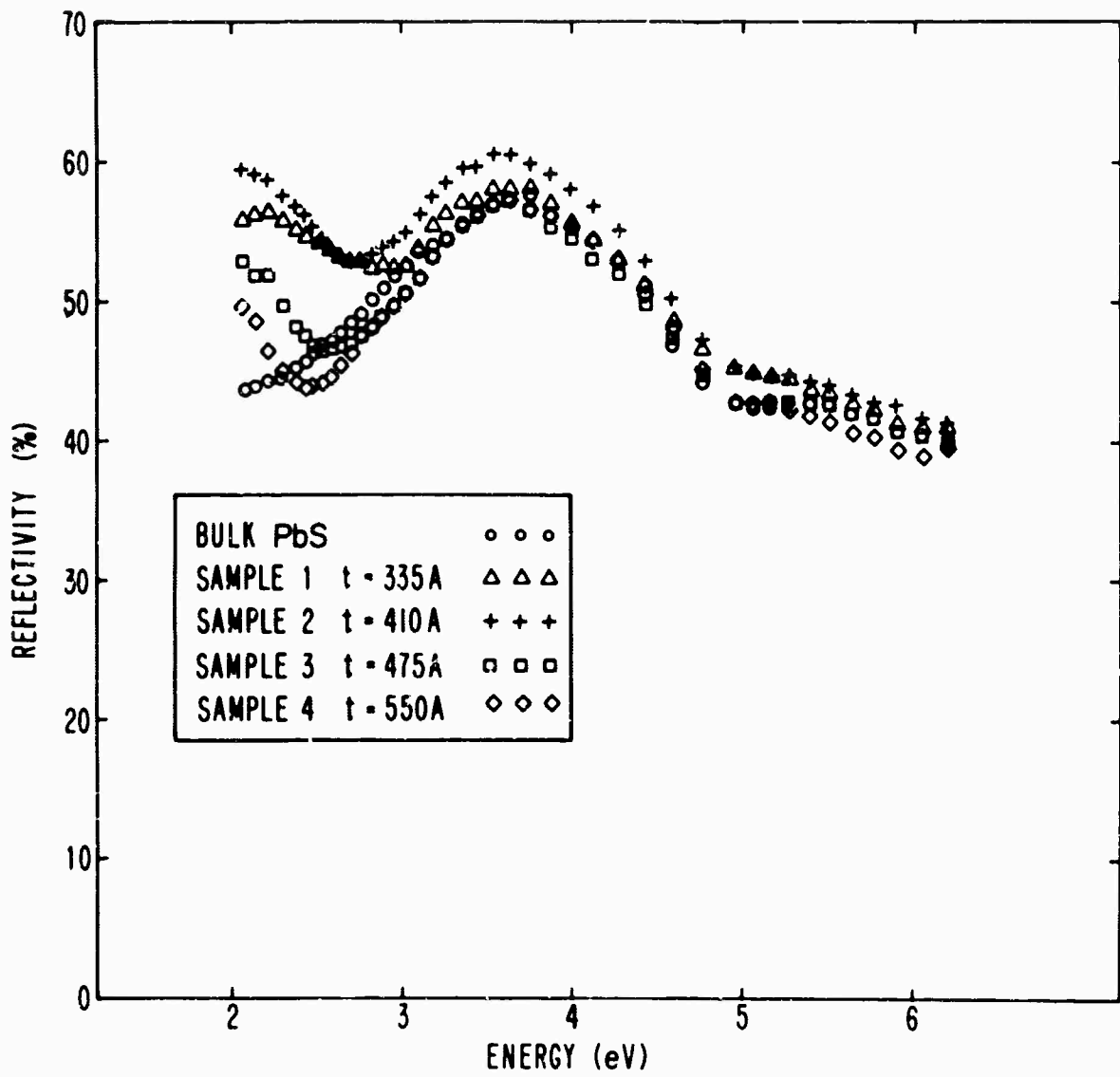


FIG. 5 REFLECTIVITY MEASUREMENTS OF BULK SAMPLE AND FILMS.

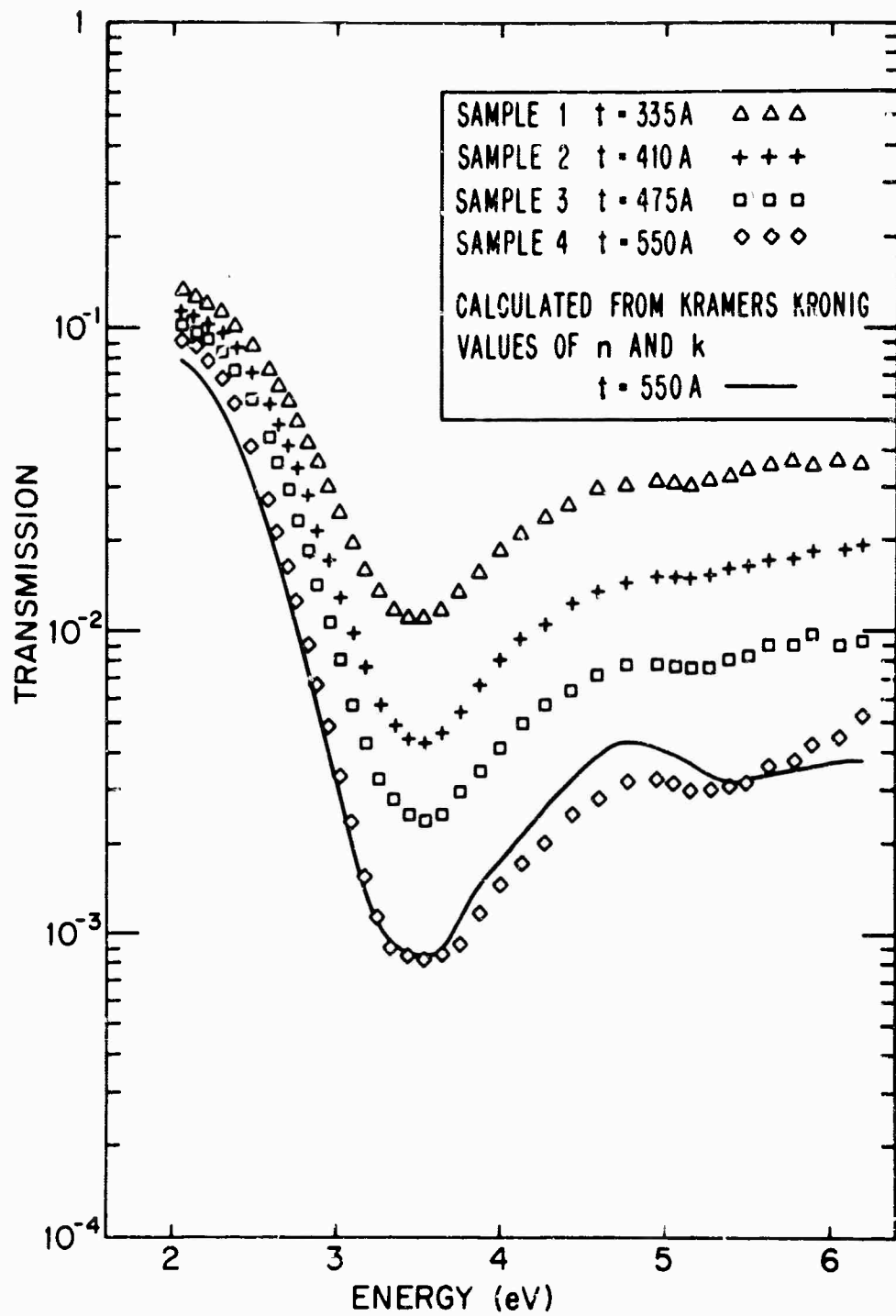


FIG. 6 TRANSMISSION MEASUREMENTS OF FILMS.

to be $\pm 5\%$ absolute. In addition, small errors can occur due to distortion of the beam by the reflecting surface of the sample. For example, the higher reflectivity of Sample 2 may not be entirely due to optical alignment. As pointed out earlier, the largest source of error is in the wavelength dependent correction applied to our data to account for differences in reflectivity occurring when the tube was turned 180° . The same correction was applied to all data and does not affect the agreement between the film reflectivities and the bulk reflectivity.

The transmission shows minima near 5.2 eV and 3.5 eV again in agreement with the results reported by Cardona and Greenaway.² The total error in transmission is estimated to be between 10 and 25%, including errors caused by scattered light from other wavelengths in the thicker samples and errors caused by imperfections in the films and film substrates. In particular, the cleavage planes of the two surfaces of the substrate can reduce the transmission and any small pinholes in the films can cause an increase in the transmission. The errors are no doubt greatest in the thicker samples near 3.5 eV where the effect of any pinholes would be the largest and above 5.4 eV where the signal to noise ratio being transmission was the smallest and where scattered light must be most significant. The effect of scattered light would be to cause the measured transmission to rise more rapidly than the true transmission between 5 and 6.2 eV, since this is the region where the light source falls rapidly in intensity with increasing energy. As one approaches 6 eV, the transmission of the thin ($\sim 3 \mu\text{m}$) NaCl and KCl substrates falls several percent, thus also distorting the transmission curves somewhat at the high energies. The measurements were made on the area of each film

appearing to have the fewest average planes and pinholes. The consistency of shape in the transmission curves as well as the consistency in the k values derived from the various films indicates that any errors due to pinholes, scattered light, etc., are probably small.

In the course of our work, we measured the transmission of 10 films on substrates of NaCl, KCl, and CaF₂. Measurements were made on a Cary 14 spectrometer and a McPherson model 225 spectrometer as well as the Jarrel Ash instrument used for the measurements of Figure 6. Considering all of the measurements made, we concluded that neither the substrates, pinholes, or scattered light has had a significant effect on the structure shown in the transmission curves. The ten transmission curves are shown in Figure 7 plotted against the wavelength in microns. The substrate material and instrument on which the measurements were taken is indicated for each film. The film on CaF₂ measured on the McPherson instrument shows a higher transmission at 3500A in relation to that at 2200A than would be expected from the other film results. The same result was obtained for this film when measured on the Cary 14 and is therefore, not a peculiarity of the McPherson instrument, but is probably due to pinholes in the film. The transmission curves of the other films agree with one another remarkably well. There are two pairs of films which have almost identical transmissions. The minimum at about 3500A is shifted to shorter wavelengths in the thinner films due to interference. It should be noted that the structure appears in all the results and thus can not be due to either the substrate or the instrument used in making the measurements.

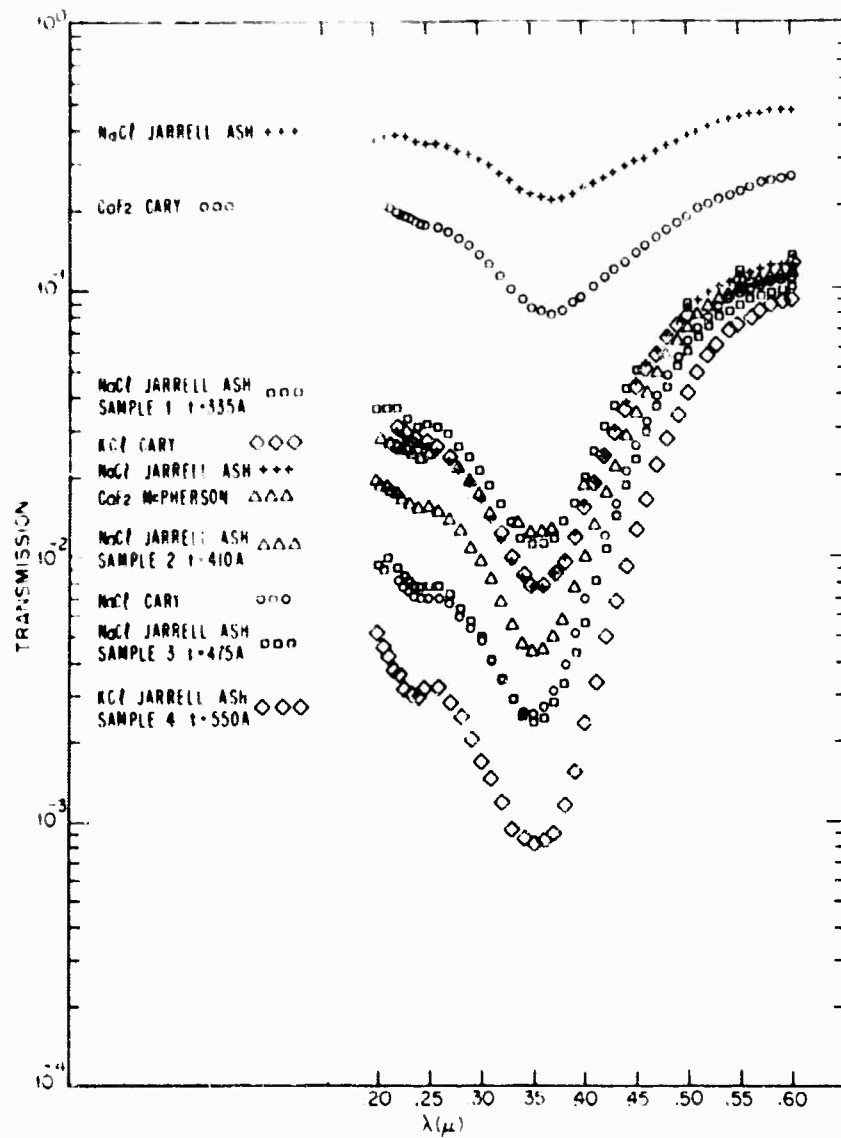


FIG. 7 TRANSMISSION MEASUREMENTS OF FILMS ON DIFFERENT SUBSTRATES. THE MEASUREMENTS WERE TAKEN ON THREE DIFFERENT OPTICAL SPECTROMETERS AS INDICATED IN THE FIGURE. FOR THE FILM ON CaF₂ MEASURED ON THE MCPHERSON, DATA WAS NOT TAKEN AT ALL WAVELENGTHS. IN TWO OTHER CASES, DATA HAS NOT BEEN PLOTTED EVERY 100A AT LONG WAVELENGTHS WHERE MANY POINTS FALL ON TOP OF ONE ANOTHER.

B. n and k from Kramers Kronig Analysis.

Grant¹³ has prepared a computer program to calculate n and k from the bulk reflectivity using the Kramers Kronig relation. n and k can be obtained from the reflectivity R and phase θ as follows:^{2, 17, 18}

$$n = \frac{(1 - R)}{1 + R - 2\sqrt{R} \cos \theta}$$

$$k = \frac{2\sqrt{R} \sin \theta}{1 + R - 2\sqrt{R} \cos \theta}$$

The phase θ is given by

$$\theta(E) = \frac{E}{\pi} \int_0^{\infty} [\ln R(E') - \ln R(E)] (E^2 - E'^2)^{-1} dE'$$

and requires the reflectivity values at all energies. The computer program approximates the integrand through each set of adjacent three points by a parabola and is such that it will accept experimental values of reflectivity at unequal energy intervals as input. The integral from 0 to a cutoff energy E_{\max} is computed by adding the contribution from each parabolic segment. Above E_{\max} the reflectivity spectrum is approximated by $R_{\max} \left(\frac{E_{\max}}{E}\right)^P$ where R_{\max} is the value of reflectivity at E_{\max} and P is an adjustable parameter, the specification of which will be discussed shortly. The integration of the phase integral from E_{\max} to ∞ has the following value:

$$\frac{1}{2n} \ln \frac{R(E)}{R(E_{\max})} = \ln \frac{E_{\max} + E}{|E_{\max} - E|} + \frac{P}{n} \sum_n (2n + 1)^{-2} \left(\frac{E}{E_{\max}} \right)^{2n + 1}$$

The sum is computed to 50 terms.

In the Kramers Kronig Analysis, our measured bulk reflectivity values were used between 2.07 eV and 6.2 eV. From 0 to 1.2 eV the reflectivity was computed from the values of n and k reported by Schoolar and Dixon,¹¹ k being assumed 0 below the gap and n extrapolated to 4.1 at 0 energy. Cardona and Greenway's² values of R were adjusted to agree with the reflectivity computed as indicated above at 1.2 eV and with our measured value at 2.07 eV to cover the range 1.2 to 2.07 eV. The values of Cardona and Greenway were multiplied by a factor to make them agree with our results at 6.2 eV and used between 6.2 and 20 eV. Above 20 eV R was extrapolated as $R = R_{20} \left(\frac{20}{E} \right)^P$. P was then adjusted to give values of k nearly equal to 0 below the energy gap and agreeing with the values of Schoolar and Dixon in the region just above the gap. The final value of P = 3 was used.

The final values of n and k obtained are shown in Figure 10. The effect of the extrapolation parameter P on the values of n and k between 2.1 and 6.2 eV is shown in Figure 8 and the effect on the values of k near the energy gap is shown in Figure 9.

The transmission of a 550 Å film on a NaCl substrate has been calculated from the Kramers Kronig values of n and k and is shown in Figure 6. The computed transmissions can be compared with that measured for the films and in particular, can be compared with the transmission of

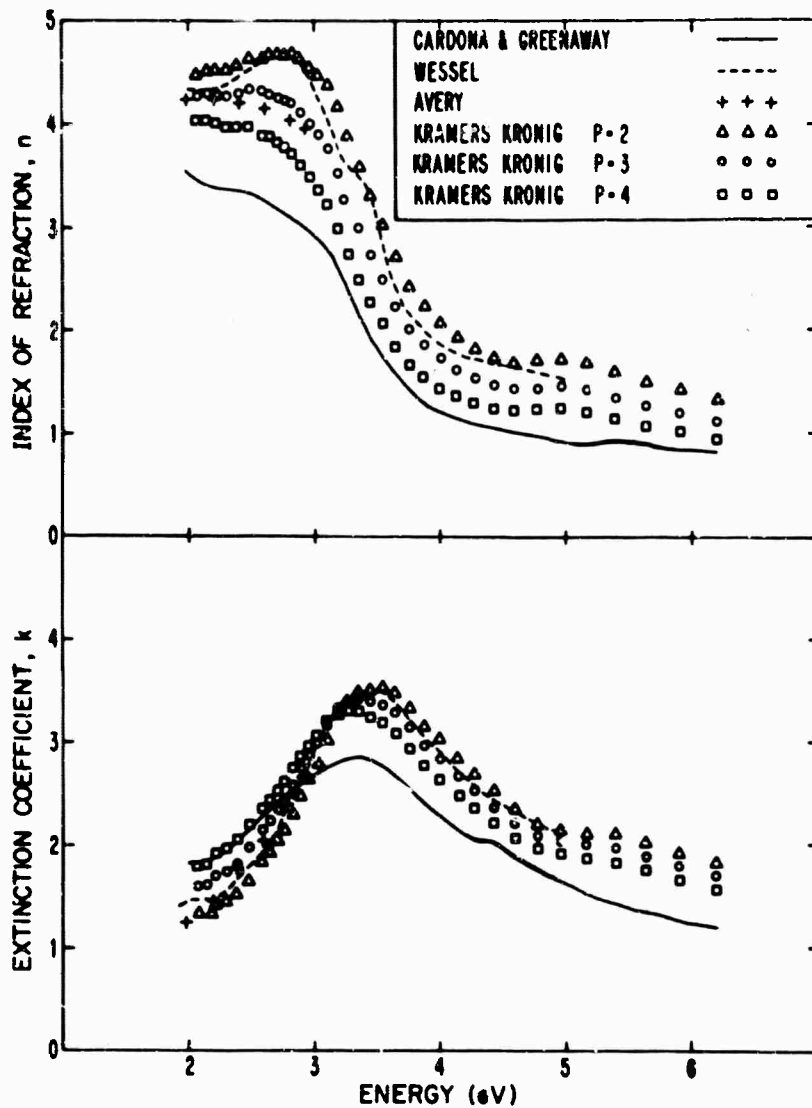


FIG. 8 n AND k FROM KRAMERS KRONIG ANALYSIS FOR VARIOUS EXTRAPOLATION ABOVE 20 eV. THE EXTRAPOLATION USED WAS

$$R = R_{20\text{eV}} \left(\frac{20}{E}\right)^P$$

WHERE P IS AN ADJUSTABLE PARAMETER. THE BEST FIT OF k TO THE VALUES OF REFERENCE 11 IN THE REGION NEAR THE ENERGY GAP WAS OBTAINED WITH $P = 3$. THE RESULTS OF CARDONA AND GREENAWAY (REF. 2), WESSEL (REF. 12) AND AVERY (REF. 19) ARE ALSO SHOWN.

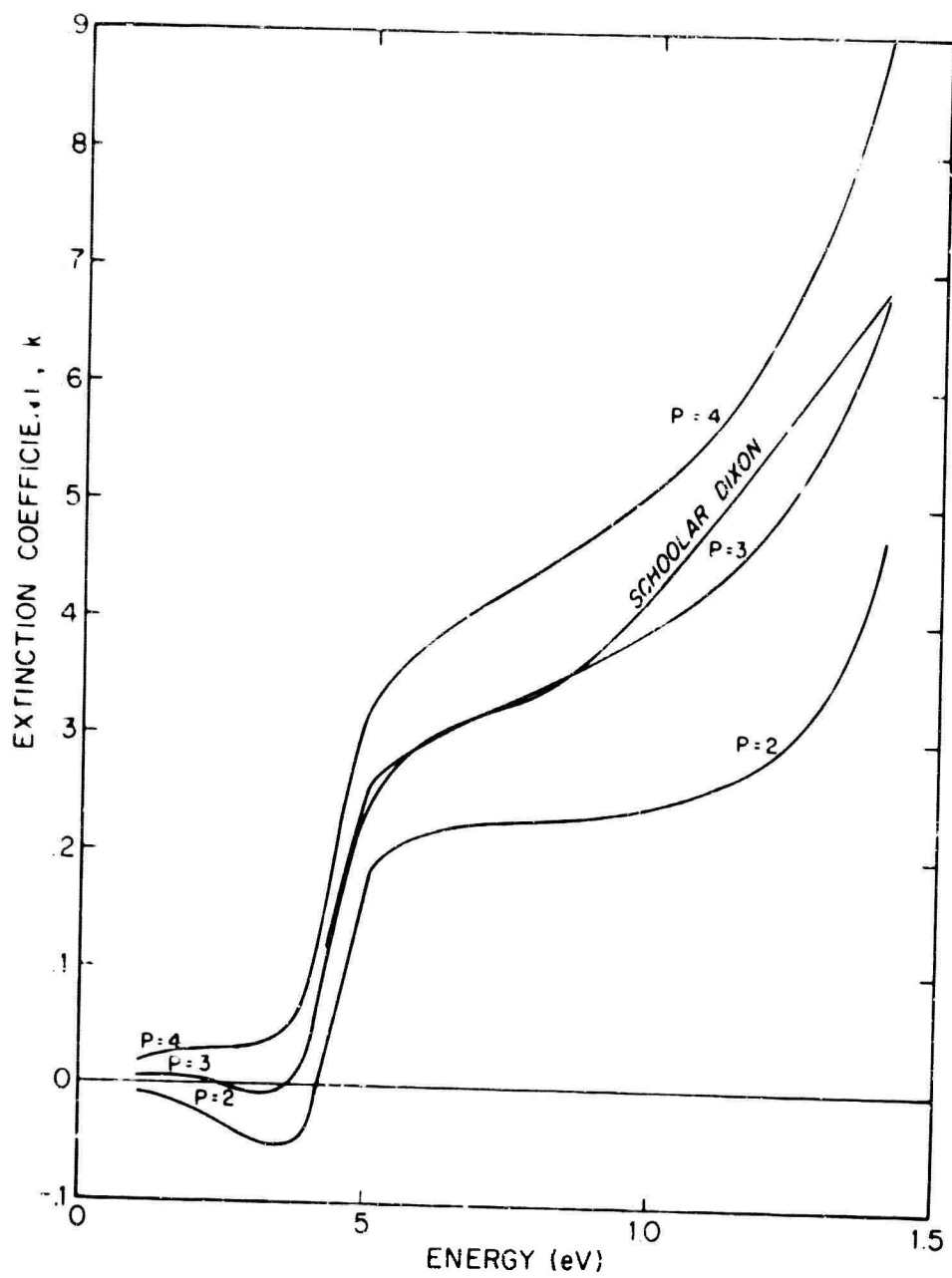


FIG. 9 THE EFFECT OF THE EXTRAPOLATION OF REFLECTIVITY ABOVE 20eV ON THE KRAMERS KRONIG VALUES OF k NEAR THE GAP.

$$R = R_{20\text{eV}} \left(\frac{20}{E} \right)^P$$

WHERE P IS AN ADJUSTABLE PARAMETER. THE RESULTS OF SCHOOLAR AND DIXON ARE ALSO SHOWN (REF. 11).

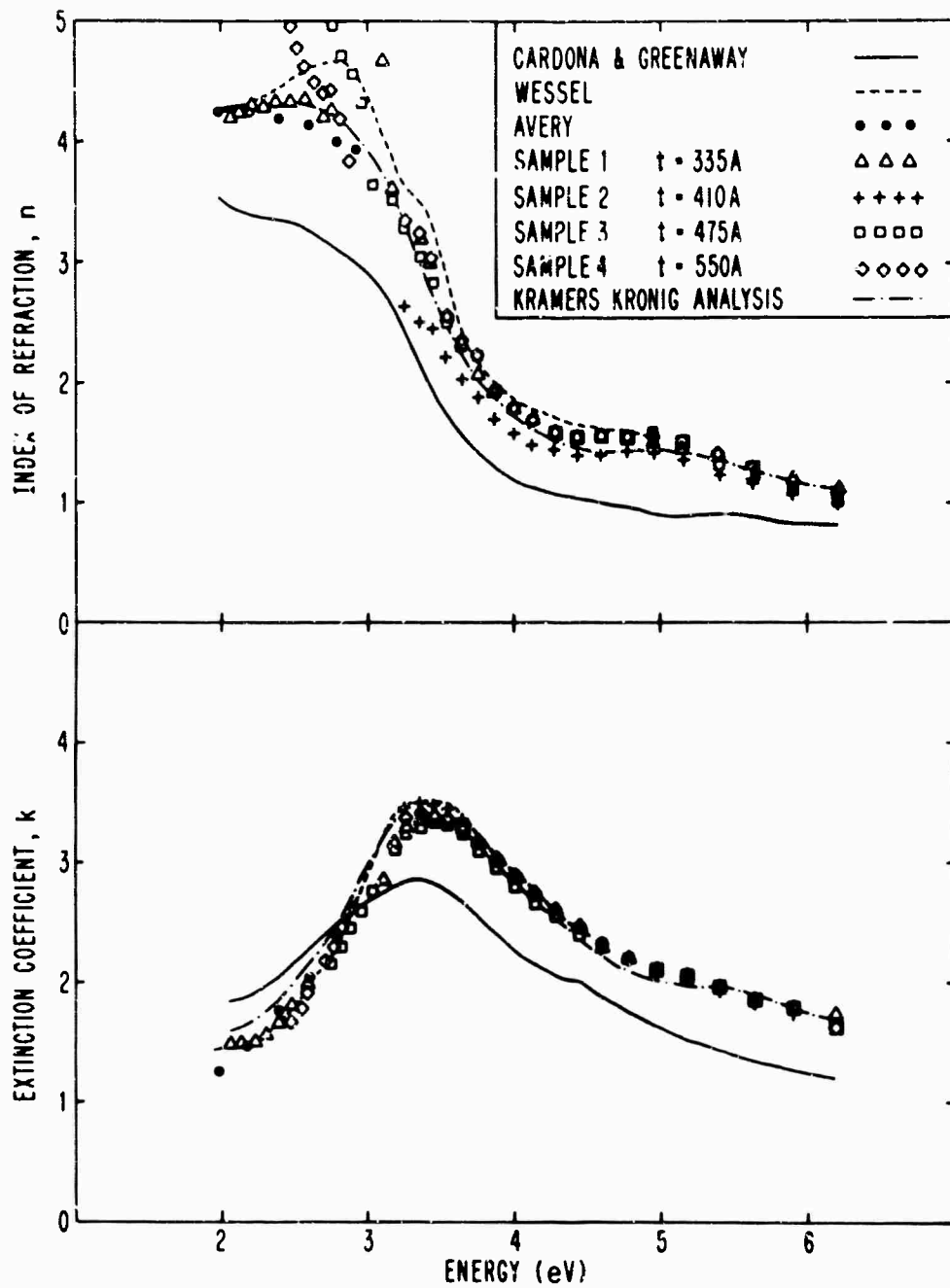


FIG. 10 THE OPTICAL CONSTANTS OF PbS OBTAINED FROM A KRAMERS KRONIG ANALYSIS OF THE BULK REFLECTIVITY AND FROM THE REFLECTIVITY AND TRANSMISSION OF THIN FILMS. THE RESULTS OF CARDONA AND GREENAWAY (REF. 2), WESSEL (REF. 12), AND AVERY (REF. 19) ARE ALSO SHOWN.

the film on KCl which has a measured thickness of 550 Å. One sees that there is reasonable agreement in the shape of the transmission curves as computed from the Kramers Kronig analysis values of n and k and the measured film transmissions. It does, however, appear that there is some error in the shape of the k curve as computed from the Kramers Kronig analysis since the transmission predicted by the Kramers Kronig values is either low at low energies or high at high energies when compared with the film results.

C. n and k from Film Reflectivity and Transmission.

n and k were computed from the measured values of R and T using a computer program written by Grant.¹³ The program uses the Newton-Raphson iterative procedure to solve the equations given by Hall and Ferguson.²¹ The equations account for multiple reflections in the film and multiple reflections in the substrate, using intensity addition for the latter. All roots of n and k lying between 0 and 10 are found. The correct physical root was taken to be the one nearest the Kramers Kronig result.

As indicated by Grant,²⁰ there is an energy range for most semiconductors where the values of n and k are such that small errors in reflectivity give quite large errors in n . Furthermore, small errors in reflectivity can in some cases result in there being no roots of n and k corresponding to the measured values of reflectivity and transmission. The energy range where this occurs in lead sulfide is in the region between ~ 2 and ~ 3.2 eV. We found less difficulty in obtaining solutions for the sample of thickness 335 Å than for the

thicker ones. In addition, a computation of the $\frac{\partial n}{\partial R}$ indicates that the errors in this energy region should be smaller for the thinner film.

The final values of n and k obtained from the films and the final values obtained from the Kramers Kronig analysis are shown in Figure 10. For three of the four films, the values of n at low energies exceeded 5 and continued to rise. The roots where $n > 5$ were not plotted. Roots reasonably near the Kramers Kronig values were obtained for the thinnest film except in the region between 2.8 and 3.2 eV.

Figure 11 shows the results of the Kramers Kronig analysis and the results from the thinnest (335 A) film along with errors in the results obtained from the film. The computed errors are based on the first order effects of errors in measured reflectivity, transmission, and thickness. The upper and lower values of n and k were computed on a computer assuming that the errors in reflectivity, transmission and thickness simultaneously cause errors in the same direction. The error bars are based on errors of $\pm 3\%$ (absolute) in reflectivity, $\pm 10\%$ (relative) in transmission, and ± 25 A in thickness. These errors are somewhat smaller than the worst case errors which we have previously indicated. However, this is offset by the fact that the absolute magnitude of the errors from the various measurements have been added in lieu of obtaining a root mean square value of the error. Furthermore, our main interest in giving the error bars is to indicate the energy region in which the errors are largest and to indicate the large effect of errors in reflectivity, transmission, and thickness on the final values of the optical constants obtained from the films.

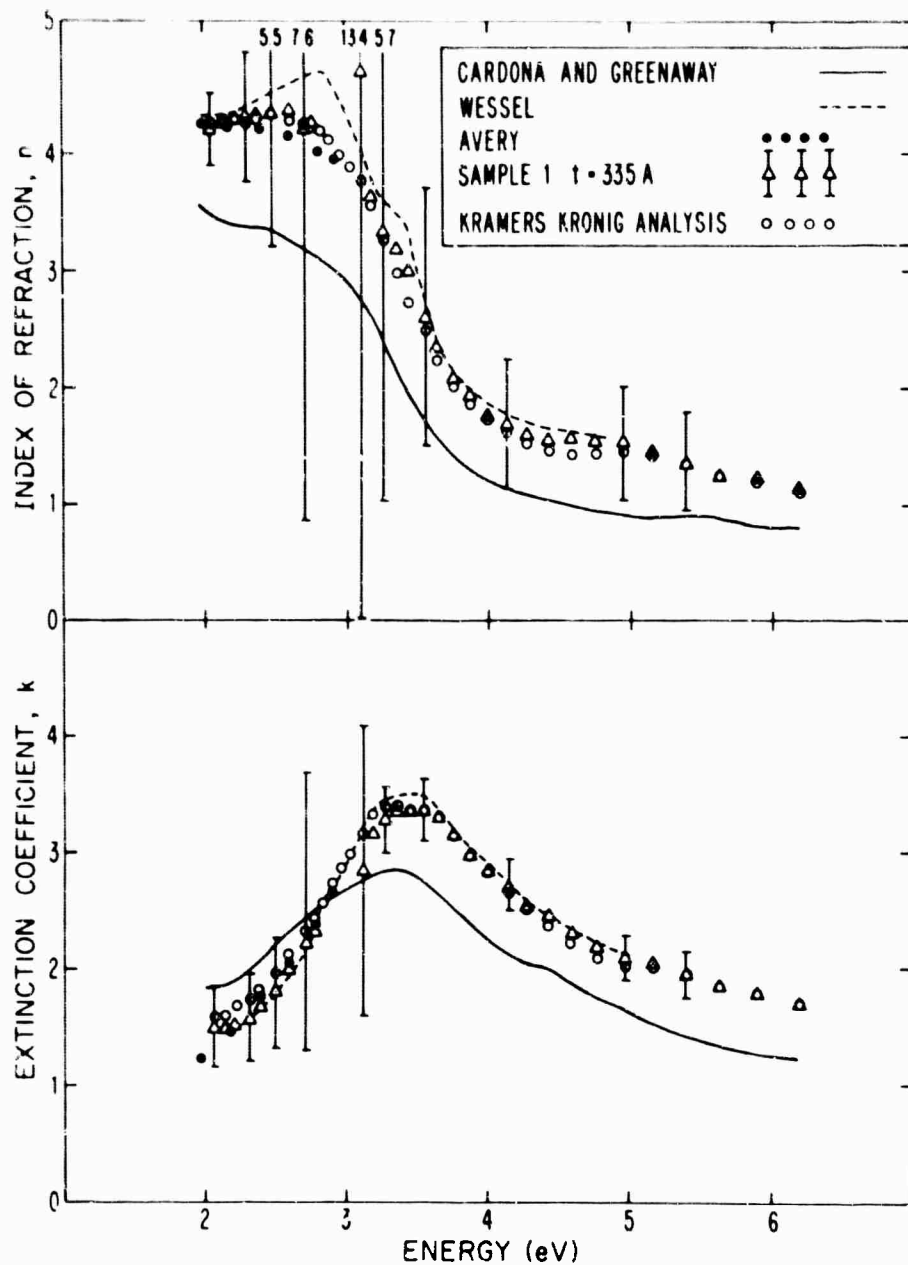


FIG. 11 THE UPPER AND LOWER BOUNDS OF THE OPTICAL CONSTANTS OBTAINED FROM SAMPLE 1 BASED ON AN ERROR OF $\pm 3\%$ (ABSOLUTE) IN REFLECTIVITY, $\pm 10\%$ (RELATIVE) IN TRANSMISSION AND $\pm 25\text{\AA}$ IN THICKNESS. THE RESULTS OF CARDONA AND GREENAWAY (REF. 2), WESSEL (REF. 12), AND AVERY (REF. 19) ARE ALSO SHOWN.

We also attempted to calculate the optical constants from the transmission measurements and thickness of two films, viz., the 335 A and 475 A films. We were, however, not successful. The values of n obtained appeared to be extremely sensitive to the thickness of the films used in the calculation. For example, a change of 5 A in the thickness of one of the films gave a large change in n . We did not check other pairs of films to determine if the particular films which we used had thicknesses such that the sensitivity of n to errors in thickness was extremely large.

In drawing conclusions from the agreement of our Kramers Kronig results, our film results, and Wessel's film results, one should keep in mind the fact that all of the results depend to some extent on the infra-red values of Schoolar and Dixon. These were used to obtain the thickness of the films and to evaluate the reflectivity extrapolation in the Kramers Kronig analysis. Errors in the thickness as a result of errors in the infra-red values of Schoolar and Dixon or as a result of errors in measuring the infra-red transmission will certainly affect the film thickness measurements in a systematic way.

The possibility also exists that errors in the infra-red values can, by changing the extrapolation at high energies required to give agreement in the infra-red, cause the Kramers Kronig results to be in error in the same direction as the film results. Furthermore, errors in the reflectivity magnitude resulting from the variation in phototube sensitivity may affect all the optical constants in the same way. Regardless of the accuracy of the optical constants, there is, however, strong evidence from the agreement of the film reflectivities with the bulk reflectivity and from the agreement in shape of the transmission curves for films of various thicknesses that the films have the same optical properties as the bulk material.

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13. ABSTRACT
 The reflectivity of epitaxial PbS films has been compared with the reflectivity of bulk PbS in the energy range 2.1 to 6.2 eV and found to agree in both magnitude and structure within a few percent at energies where interference effects can be neglected. The transmission of several films with thicknesses varying from 335 A to 550 A has been measured and the structure and shape of the spectra shown to be the same for the films with different thicknesses. The reflectivity of bulk PbS between 2.1 and 6.2 eV has been combined with measurements made by other workers outside of this range to compute optical constants from the Kramers Kronig relation. The optical constants obtained in this manner appear to agree quite well with those obtained from the reflectivity and transmission of the films, considering the experimental difficulties experienced in measuring film thickness and the absolute magnitude of the reflectivity.

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