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DEPARTMENT OF THE ARMY
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FORT BELVOIR, VIRGINIA

RESEARCH AND DEVELOPMENT
BAUSCH & LOMB INCORPORATED

CONTRACT DA-44-009-AMC-124(T)

15 MARCH 1963 - 15 JUNE 1963

INFRARED COATING STUDIES
FIRST QUARTER REPORT 1963

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INTRODUCTION

The first section of this report describes the enhancement of reststrahlen high reflectance bands with thin films. Both calculated and measured results are given for several film combinations. The second section investigates the possibility of replacing the metal films in metal-spacer-metal filters with reststrahlen materials. The last section extends some previous work done on the effect of crystallite size on the infrared dispersion of LiF.

Section I - Enhanced Reststrahlen

For many years the reflectance of metals has been enhanced with thin films. The design criteria used there may be applied to the enhancement of reststrahlen bands. In order to calculate the reflectance of such film combinations it was necessary to write a new program for the IBM 1620 computer. This program allowed the use of dispersive materials in thin film calculations. It is, however, necessary to know for each material the dispersion parameters defined by the Drude formulas,

$$n^2 - k^2 - n_\infty^2 = \sum_j \frac{A_j(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \omega^2 q_j^2} \quad (1)$$

$$2nk = \sum_j \frac{A_j \omega q_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 q_j^2} \quad (2)$$

Unfortunately, the program does not handle dispersive substrates. This difficulty is overcome by using a thick opaque dispersive film as the effective substrate, but the approximation is good only in the region of opacity.

The dispersion parameters used in the calculations are listed in Table 1. The values used for CaF_2 and BaF_2 are those recently reported by Kaiser, Spitzer, Kaiser, and Howorth.² The parameters of LiF were determined under the previous contract.³ It was, however, necessary to calculate the dispersion parameters of MgO . This was done in the standard way. The reflectance of massive MgO was fit by finding the appropriate parameters in the Drude dispersion expressions and application of the Fresnel formula. Such a fit using only a single term in the summation is shown in Figure 3. The corresponding values of the index of refraction are also shown in this figure.

Infrared Dispersion Parameters of Several Ionic Crystals

	A_1	A_2	W_1	W_2	ϵ_1	ϵ_2	N
BaF ₂	5.97×10^{27}	1.91×10^{26}	3.46×10^{13}	5.22×10^{13}	6.92×10^{11}	1.57×10^{13}	1.47
CaF ₂	9.8×10^{27}	1.52×10^{27}	4.83×10^{13}	6.17×10^{13}	8.7×10^{11}	2.15×10^{13}	1.43
LiF	2.43×10^{28}	1.03×10^{27}	5.79×10^{13}	9.4×10^{13}	3.75×10^{12}	1.58×10^{13}	1.38
MgO	3.58×10^{28}	--	7.24×10^{13}	--	6.0×10^{12}	--	1.72

TABLE 1

A slight change in the notation used to describe the film combinations is necessary. For example, consider the combination

$$G(.8D)(1.0H)(.8D)A \text{ at } \lambda = 20\mu$$

where D is a dispersive material and H has a real, non-dispersive index. The coefficient of D is h/λ where h is the physical thickness of the layer and λ is, as indicated, 20μ . The coefficient of H is the number of quarter waves at λ equal to 20μ , i.e., $4nh/\lambda$.

The dotted lines in Figures 1, 2, 4, and 5 show the calculated reflectance of a single layer of germanium on CaF_2 , BaF_2 , MgO , and LiF respectively. The thickness of the germanium film was chosen to give constructive interference at the wavelength indicated at the top of the figure. The reflectance is significantly enhanced in all cases. It is perhaps somewhat surprising that the region of enhancement is so broad. The reflectance does not drop until the immediate neighborhood of destructive interference is reached. Consider, for example, the minima in the reflectance of enhanced LiF (Figure 5). At the enhancing wavelength, 20 microns, the germanium film must be slightly thicker than a quarter wave to compensate for the negative phase shift at the Ge-LiF interface. At approximately 13 microns the Ge-LiF interface phase shift is zero and the film is a half wave thick, resulting in no change in reflectance. At 33 microns the positive phase shift due to the

film thickness is exactly equal to the negative phase shift at the Ge-LiF interface, resulting in destructive interference.

Measurements of reststrahlen enhanced with a single layer of germanium proved somewhat disappointing. The reflectance was down considerably from the calculated values for the two materials coated, CaF_2 and LiF (Figs. 1, 5). This was undoubtedly due to absorption in the germanium film. This absorption was dependent on the evaporating conditions. Slow rates of evaporation and high substrate temperatures will probably produce films with fewer defects and, therefore, with fewer free electrons to absorb energy. No systematic investigation was made of this germanium absorption.

Calculations were made of a two layer enhancement of the reststrahlen of LiF. The low index material used was PbCl_2 ; the high index material, germanium. Figure 6 shows that this construction brought the reflectance up to 98%. The PbCl_2 , incidently, antireflects the rear surface of the germanium film at about 10 microns. This construction was attempted several times experimentally. Although the resulting enhancement varied considerably from sample to sample, it was possible to closely approach the calculated values (Fig. 6).

A serious disadvantage is introduced if these high reflectance bands are to be used for filtering. Normally

the reflectance is only a few percent on the short wavelength side of the band. After enhancement with germanium it is seen that the relatively good background is destroyed. The background is lowered, though, on the immediate long wavelength side of the band. In an effort to improve the short wavelength background a third layer was added to the combination. The thickness of this layer was chosen to anti-reflect the first surface of the germanium film at 11 microns. Figure 7 shows the calculated and measured results. The peak at 11 microns was successfully anti-reflected, and the short wavelength side of the high reflectance band was lowered slightly. Normally multiple reflection techniques are used in reststrahlen filtering. Figure 8, for example, shows the result after three reflections off LiF. The short wavelength background is excellent, .0001%. The long wavelength background is rather poor and the reflectance band averages only 55%. The result after two reflections off LiF with a two layer enhancement and one reflection off unenhanced LiF is also shown in Figure 8. Although the excellent short wavelength background has been destroyed, the average value in the high reflectance band is raised to 75% and the long wavelength background is significantly lowered.

Section II - Reststrahlen Interference Filters

The usefulness of a metal in a metal-spacer-metal interference filter is determined by the ratio k/n , where k is

the imaginary part of the index and n is the real part. For the ideal metal ($n \rightarrow \infty$) this ratio is infinity. For aluminum in the visible the ratio is about 10. This ratio of 10, in fact, sets the limit for usable metals in interference filters. As wavelength increases, k/n approached 1 for all metals. At 20 microns there are no known metals suitable for use in interference filters. In the region of reststrahlen dispersion the ratio of k/n for a LiF film evaporated onto a substrate at 300°C is between 5 and 10. This borderline ratio suggest the possibility of replacing the metals with reststrahlen materials. Using the computer program mentioned in Section I it was possible to calculate the transmission of a filter so constructed.

The dispersion parameters of the LiF film were calculated in a previous report.³ The spacer layer was assumed to have an index corresponding to that of PbCl_2 , 1.8. The substrate was KBr with an index of 1.46. Figure 9 shows that the calculated transmission of 3 and 5 layer first order filters peaked at 23 microns. Figure 10 shows the transmission of the same combinations with the spacer layer thickness chosen for third order interference. Filters with such low peak to background ratios are not desirable, particularly in the infrared where it is necessary to deal with very low intensities.

The problem of improving the filter might be approached in the following manner. k/n for a thin film of LiF is

considerably lower than that for a single crystal of LiF. This is thought to be due to a crystallite size effect. If the indices of the film could be made to more closely approximate those of a single crystal, a little more interesting filter could be fabricated. There is, of course, also the possibility of finding a reststrahlen material more suitable than LiF.

Section III - Effect of Crystallite size on the Infrared Dispersion of LiF - Part II

A study of the effect of crystallite size on the infrared dispersion of LiF was reported in the First Quarterly Report of 1962. In this study it was necessary to make the films opaque in the region of interest because computational facilities were not available for interference effects in dispersive thin films. Now that such facilities are available the results of previous work may be tested with the thinner films.

A brief review of the previous work might be helpful. Six micron thick films of LiF were evaporated onto glass. The infrared reflectance was measured at normal incidence. This empirical reflectance curve was fit with a theoretical curve obtained by finding the appropriate parameters in the Drude dispersion expression and application of the Fresnel formula. The size of the crystallites composing the film were increased by increasing the temperature of

the substrate during deposition. The following correlation was found to exist between crystallite size and Drude dispersion parameters. As the crystallites became smaller;

- a) the damping (g_1 , g_2) in both terms increased,
- b) the strength of the main resonance (A_2) became slightly smaller,
- c) the strength of the secondary resonance (A_1) rapidly increased.

The crystallite size of an evaporated film is dependent not only on substrate temperature, but also the thickness of the film. In this experiment the crystallite size was varied by varying the film thickness. The crystallite size of the films has been determined using electron microscopy. The technique used for making carbon replicas of the surface is exactly the same as described in the Second Quarter Report, 1962. Figure 11 shows a series of electron micrographs of these replicas for several film thicknesses. The increase in crystallite size with increasingly thick films is evident. Since all films were evaporated onto a substrate at room temperature, the surface structure is not smoothed out as it was at higher temperatures in the previous experiment. If it is assumed that the average dimension of an exposed face is a measure of crystallite size then Figure 12 shows the dependence of size on film thickness. This dependence appears to be linear for relatively thin films. The growth of the crystallites appears to saturate after they reach 4000-

5000 Å in size.

Thin films of LiF were evaporated onto KRS-5. The transmission of these samples was measured, and the appropriate corrections were made for the second surface reflection of the substrate. The corrected transmission of samples of several different thicknesses is shown in Figure 13.

Using the computer program mentioned above an attempt was made to fit these transmission measurements by a suitable choice of the dispersion parameters in a two term Drude expression. The thicknesses of these films were known from transmission measurements made in the near infrared. It is not surprising that the parameters determined for single crystal LiF³ do not result in a fit of the transmission curves of these small crystal films (Fig. 14).

Figure 15 shows the transmission calculated using the dispersion parameters obtained from the fit of the reflectance of the 6 micron thick films evaporated onto a substrate at room temperature.³ These curves should correspond to the transmission of films with 5000 Å crystallites. Although the size of the crystallites in the films used here is smaller, it is perhaps surprising that these curves fit the data so poorly. A fairly good fit to the transmission data is made when the parameters indicated in Figure 16 are used. This presents an even more difficult problem. The correlations found previously between crystallite size and Drude dispersion parameters, when extra-

polated to smaller crystallites, should yield fairly good parameters. The parameters used in Figure 16 do not follow this trend. Moreover, the parameters used to fit the transmission data do not result in a fit of the previous reflectance data (Fig. 17). They also give a long wavelength index of refraction almost twice as large as it should be.

An explanation for all these difficulties has not been found. It is possible that the Drude dispersion formula is not applicable to this problem. Born and Huang have developed a dispersion expression based on a quantum mechanical perturbation calculation (eq. 2,3).

$$n^2 - k^2 - n_\infty^2 = \left(\frac{A}{\omega_0 + \omega} \right) \frac{\omega_0 - \omega + g^2/2\omega_0}{(\omega_0 - \omega)^2 + g^2} \quad (3)$$

$$2nk = \left(\frac{Ag}{2\omega_0} \right) \frac{1}{(\omega_0 - \omega)^2 + g^2} \quad (4)$$

In these equations g is a function of w . $g(w)$ may be calculated if the lattice vibrational spectrum is known. This is a considerable improvement over the g in the Drude expression, which is just an arbitrary velocity proportional damping constant with little physical significance. It can be noticed that both sets of expressions have the same limit when g goes to zero. This might explain why the Drude formula is so good for single crystal LiF. For thin films, though, it appears that g increases considerably, and it may be necessary to use the more exact Born-Huang expression.

ACKNOWLEDGEMENTS

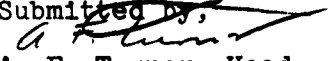
R. T. MacIntyre is gratefully acknowledged for writing the computer program enabling the calculations on thin film combinations with dispersive materials. Thanks are due to Miss M. Vetter for taking the electron micrographs, to L. Bartle for fabricating the enhanced reststrahlen plates, and to J. Masso for his valuable general assistance in the size effect experiments.

REFERENCES

- 1) Bilz, Genzel, and Happ, "Zur Ultrarotdispersion der AlkaliHalogenide," Z. Physik, Vol. 160, 1960, P. 535.
- 2) Kaiser, Spitzer, Kaiser, and Howarth, "Infrared Properties of CaF_2 , SrF_2 , and BaF_2 ," Phys. Rev., Vol. 127, 1962, p. 1950.
- 3) Martin, First Quarter Report to Fort Belvoir, Contract DA-44-009-ENG-4954, 1962.
- 4) , Second Quarter Report to Fort Belvoir, Contract DA-44-009-ENG-4954, 1962.

This report was prepared by T. P. Martin

Submitted by,


A. F. Turner, Head
Optical Physics, Research
and Development

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF CaF_2

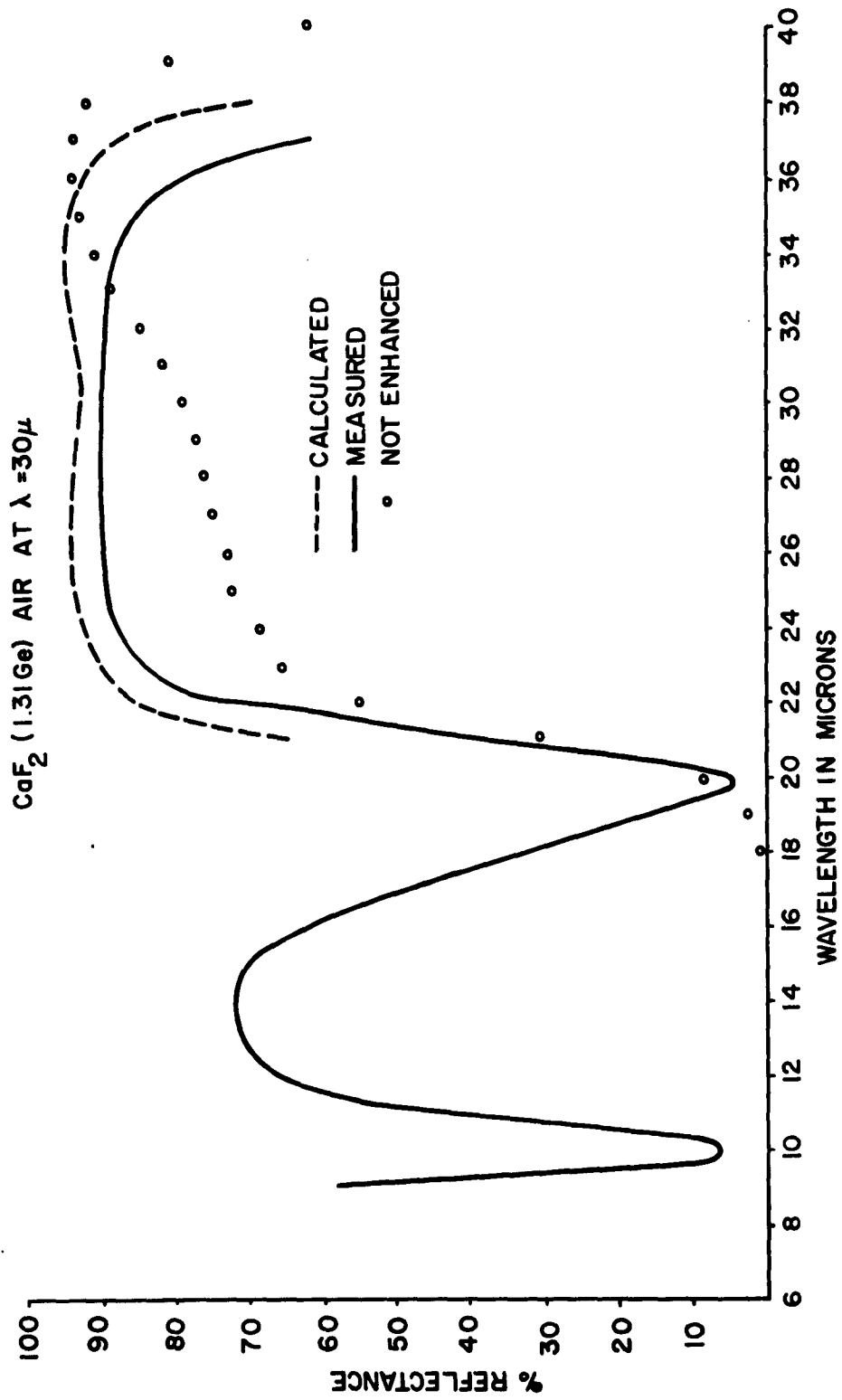


FIG. 1

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF BaF₂

BaF₂ (1.21Ge) AIR AT $\lambda = 42\mu$

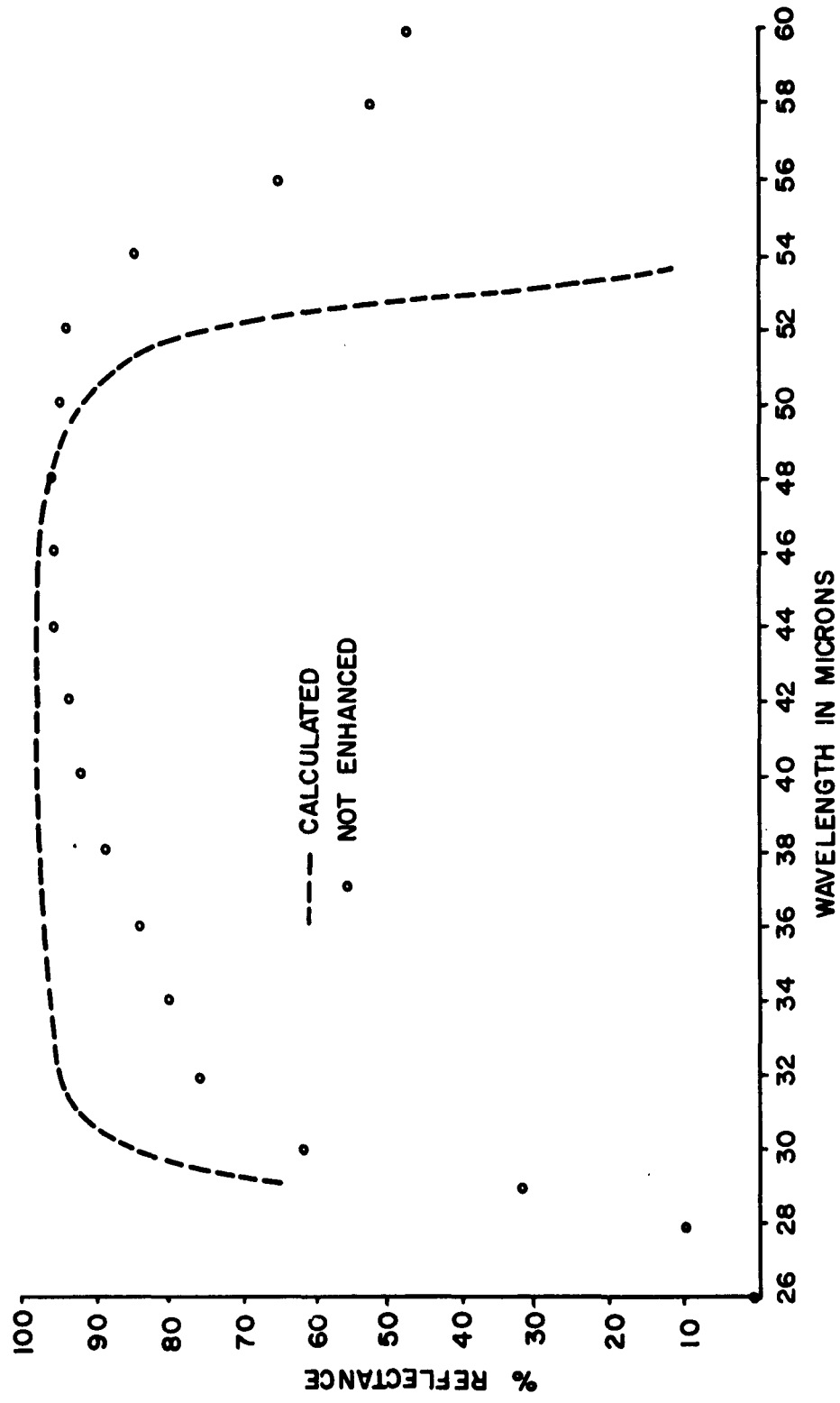


FIG. 2

REFLECTANCE AND DISPERSION OF MgO IN THE RESTSTRAHLEN REGION

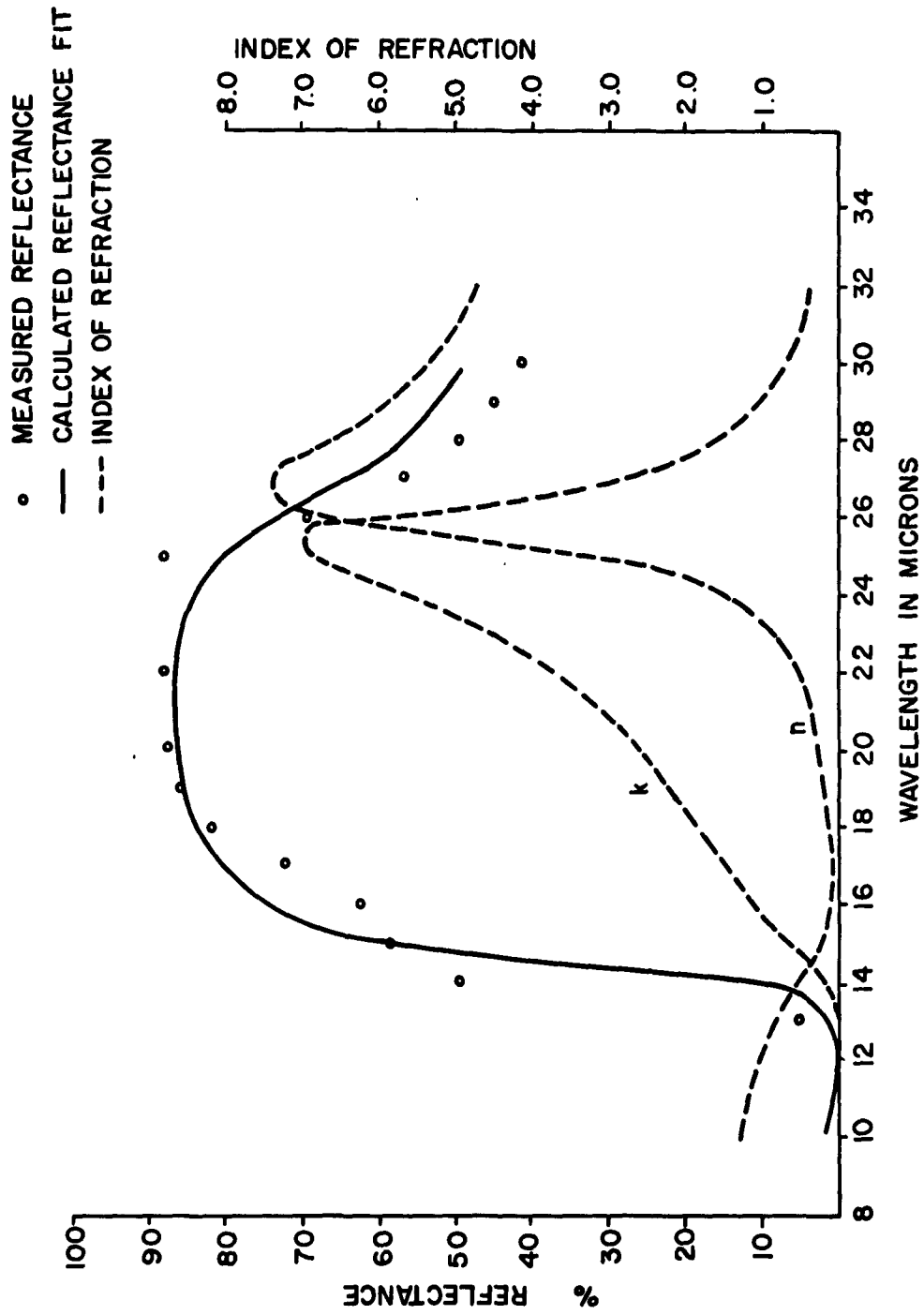


FIG. 3

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF MgO

MgO (1.29 Ge) AIR AT $\lambda = 18\mu$

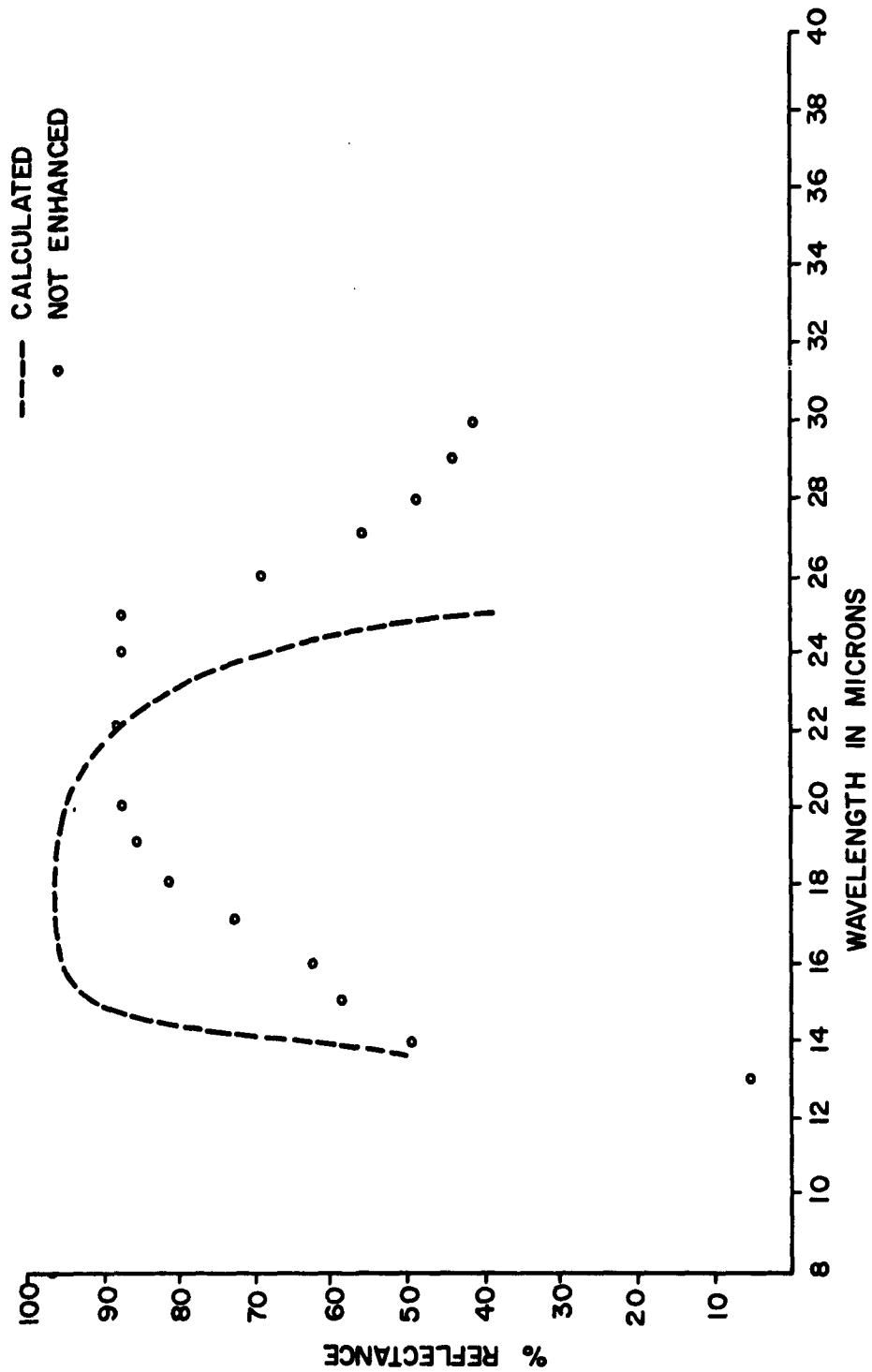


FIG. 4

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (1.26Ge) AIR AT $\lambda = 20$

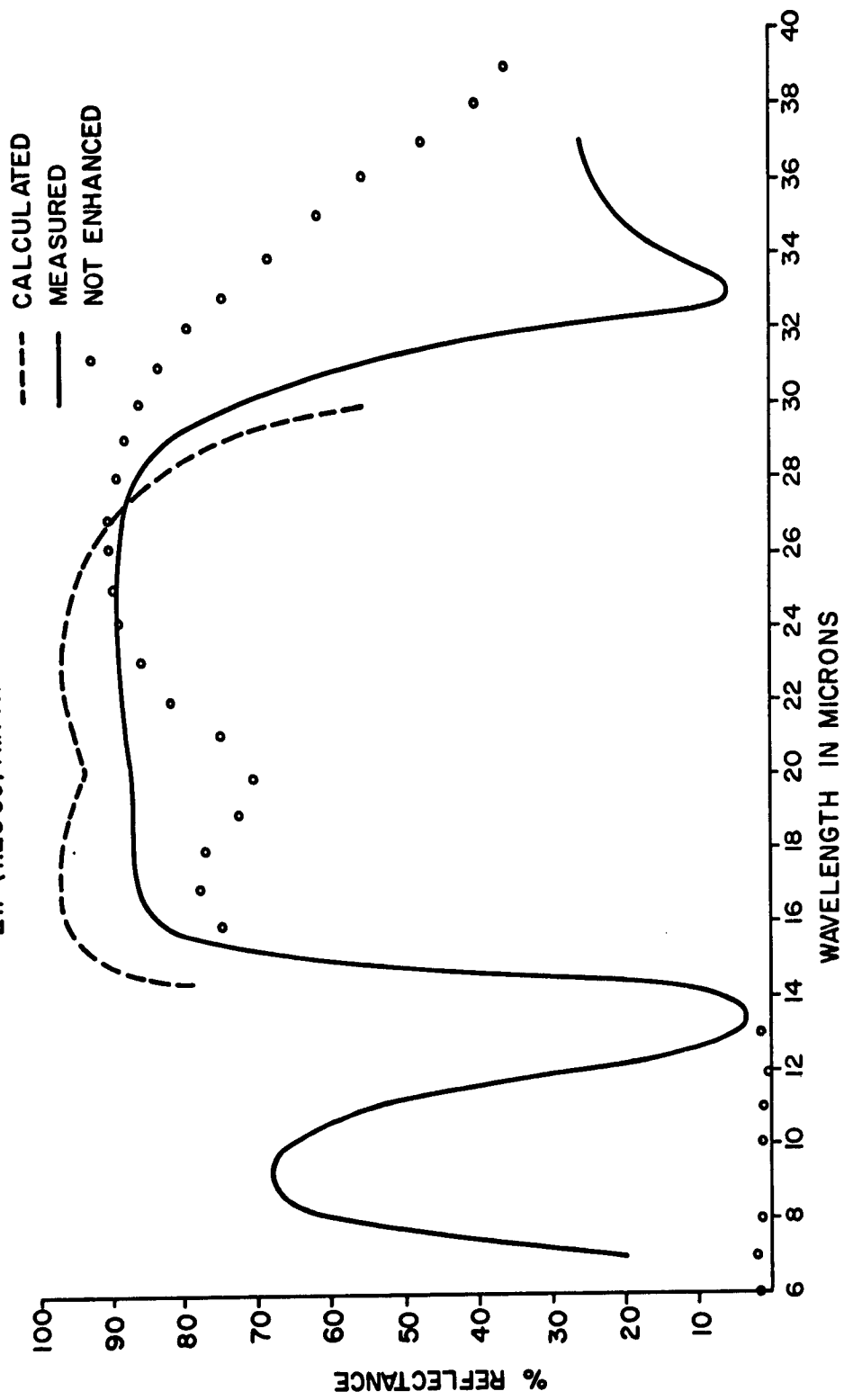


FIG. 5

TWO LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (.47 Pb Cl₂) (1.0 Ge) AIR AT $\lambda = 20$

--- CALCULATED
— MEASURED
o NOT ENHANCED

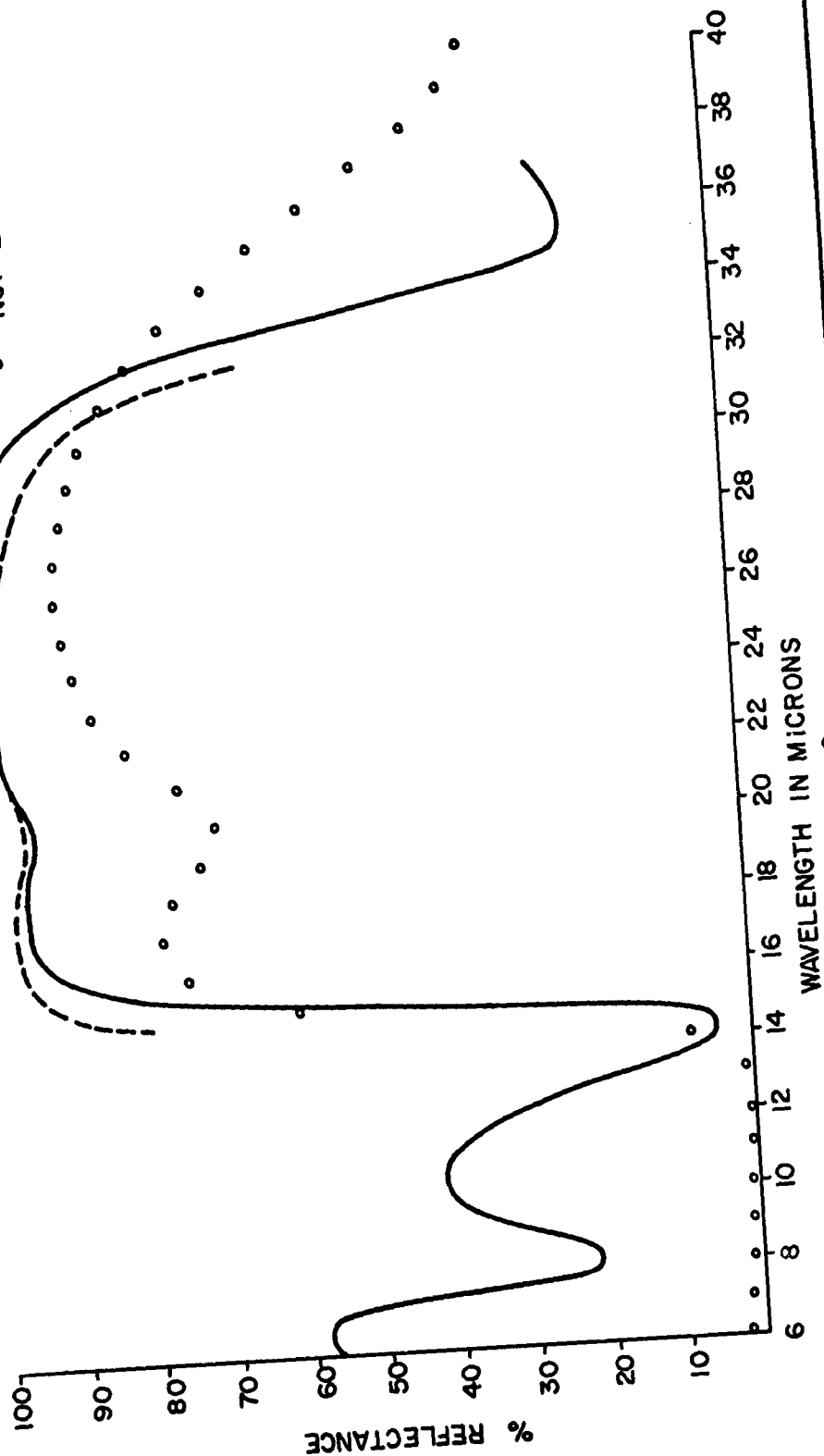


FIG. 6

THREE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (.47 PbCl₂)(1.0Ge)(.55 PbCl₂)AIR AT $\lambda = 20$

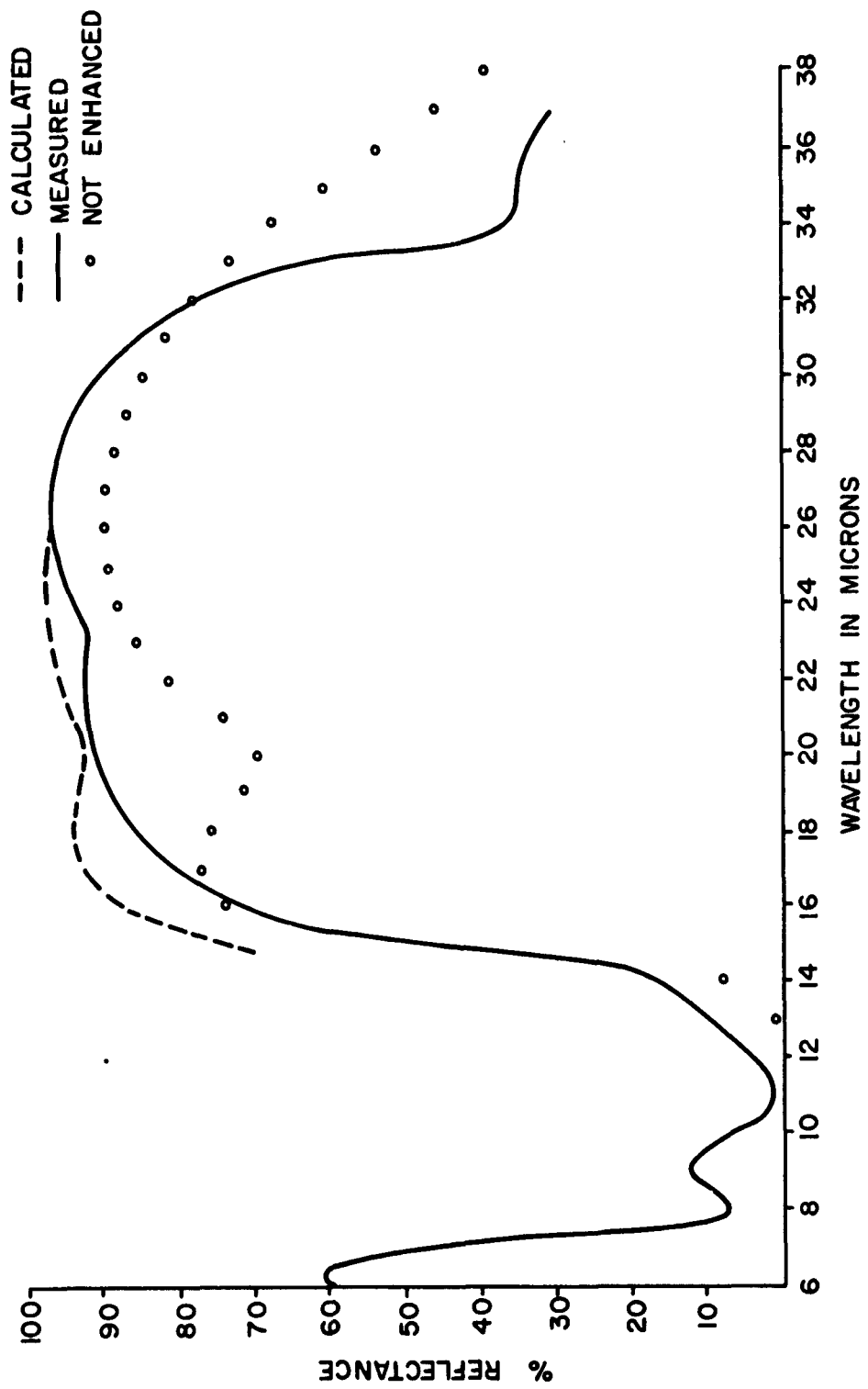


FIG. 7

RESTSTRAHLEN FILTERING WITH ENHANCED LiF

$$\begin{aligned} & \text{---} (R_{LiF})(R_{ENLiF})^2 \\ & \text{---} (R_{LiF})^3 \\ & \text{.} (R_{LiF}) \end{aligned}$$

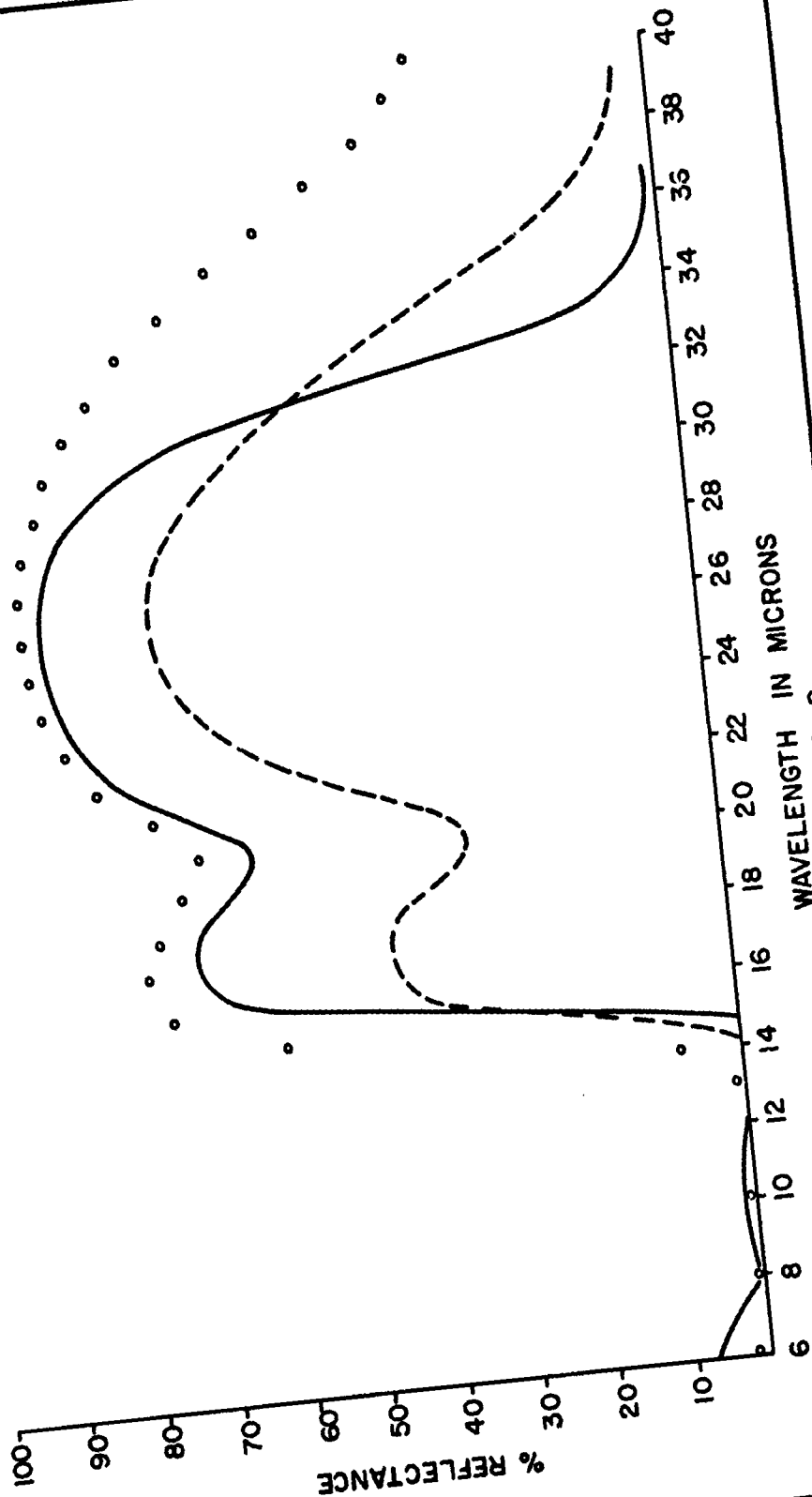


FIG. 8

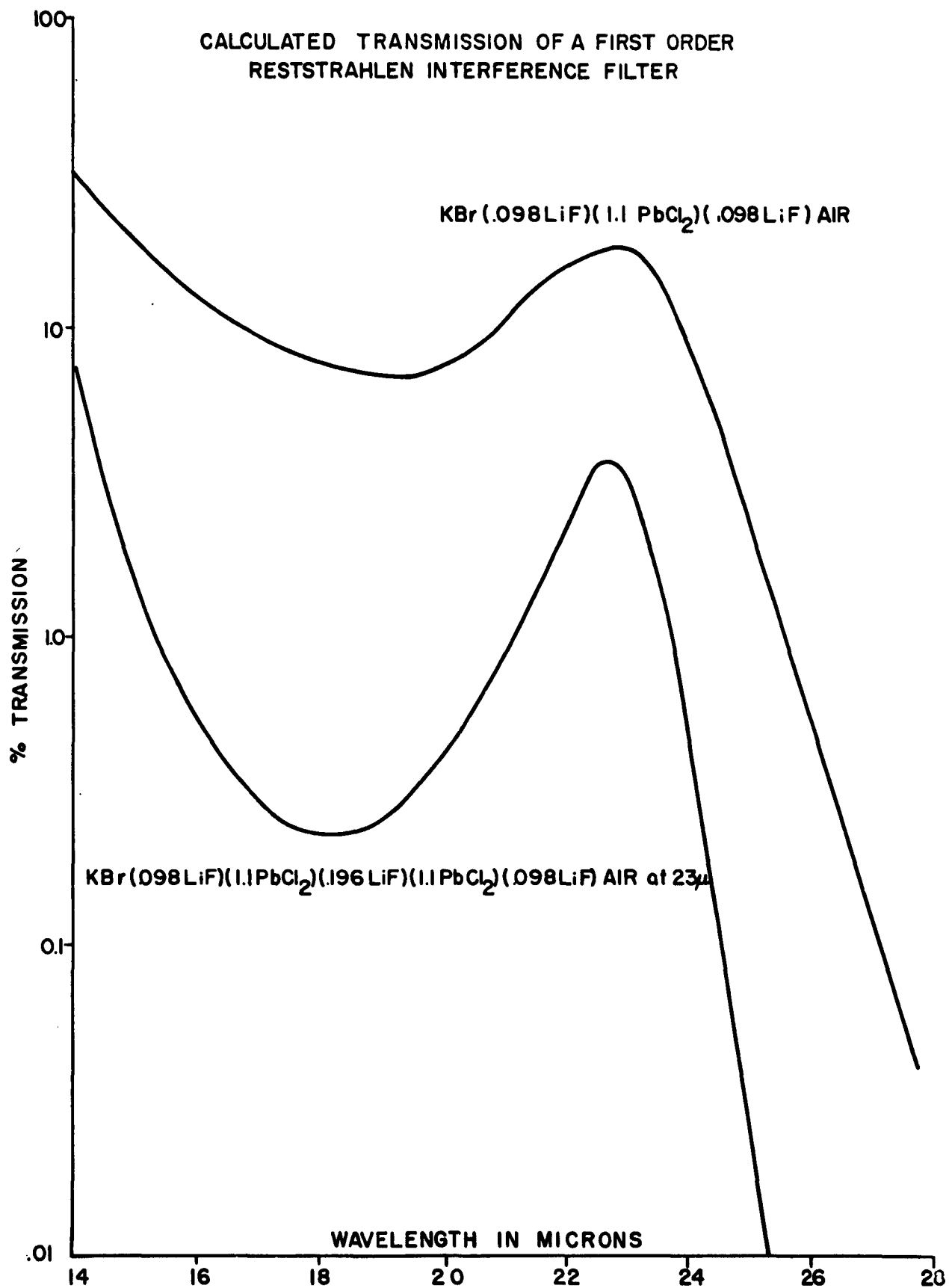


FIG. 9

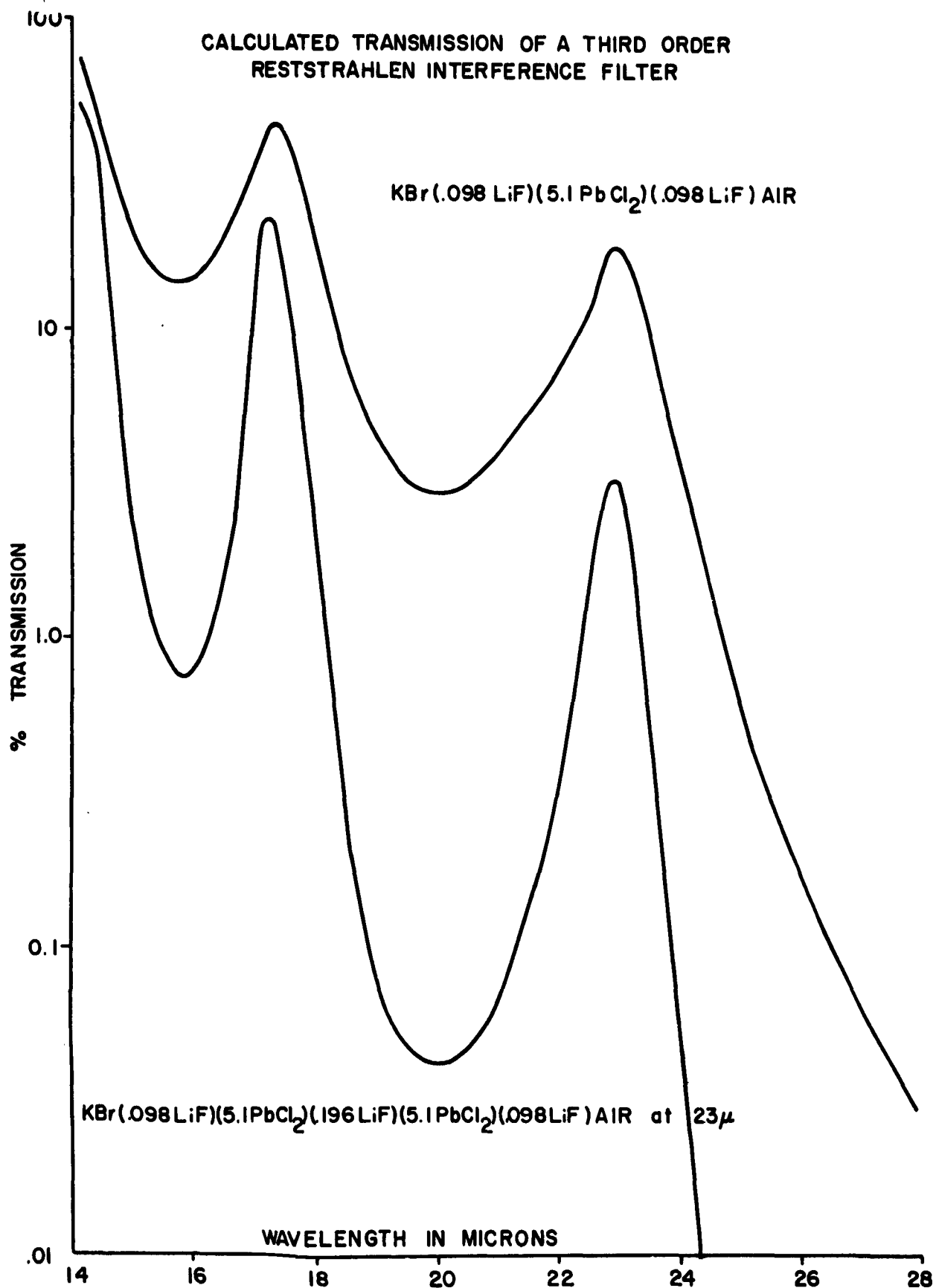


FIG. 10

ELECTRON MICROGRAPHS OF LiF THIN FILMS
OF INDICATED THICKNESS

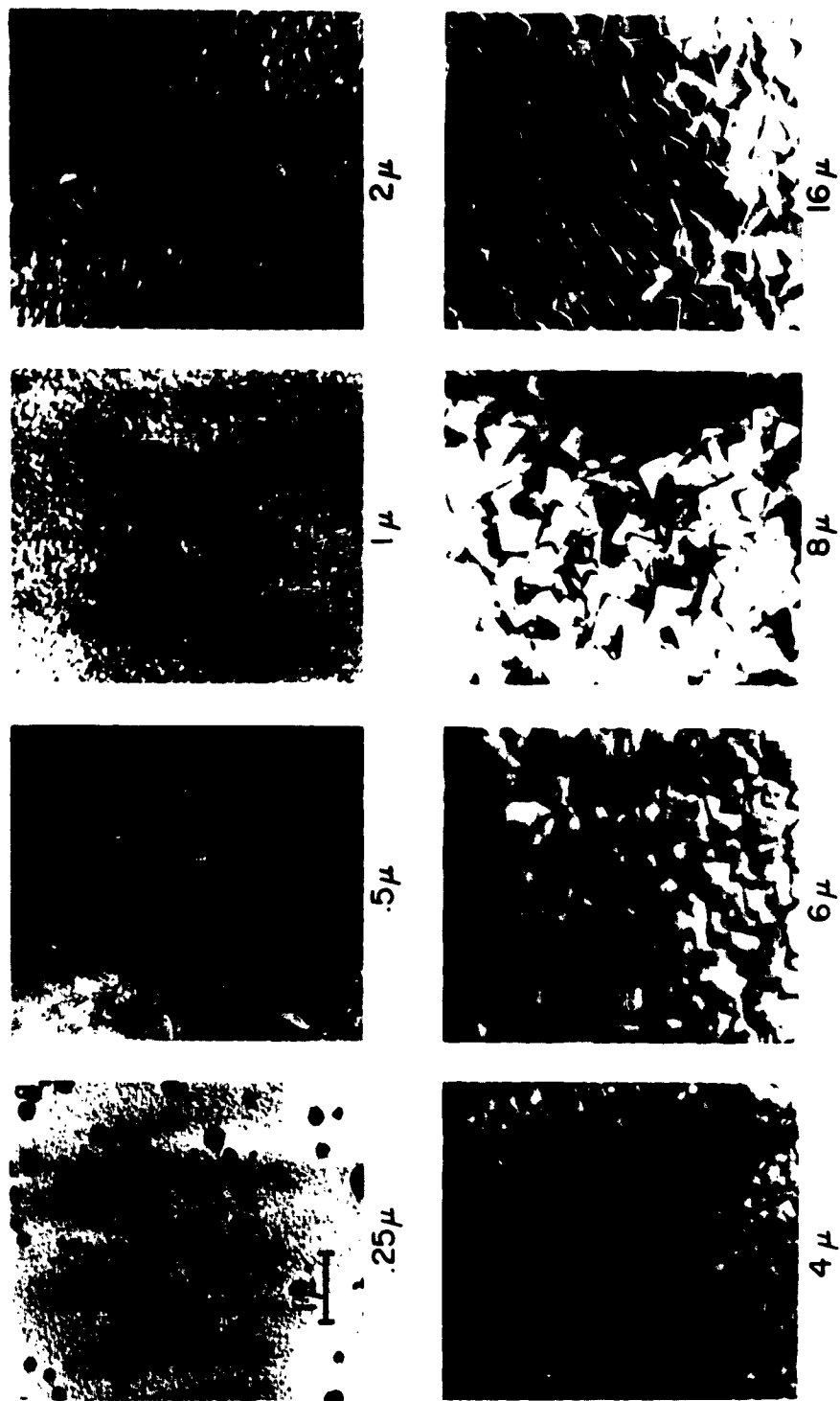


FIGURE II

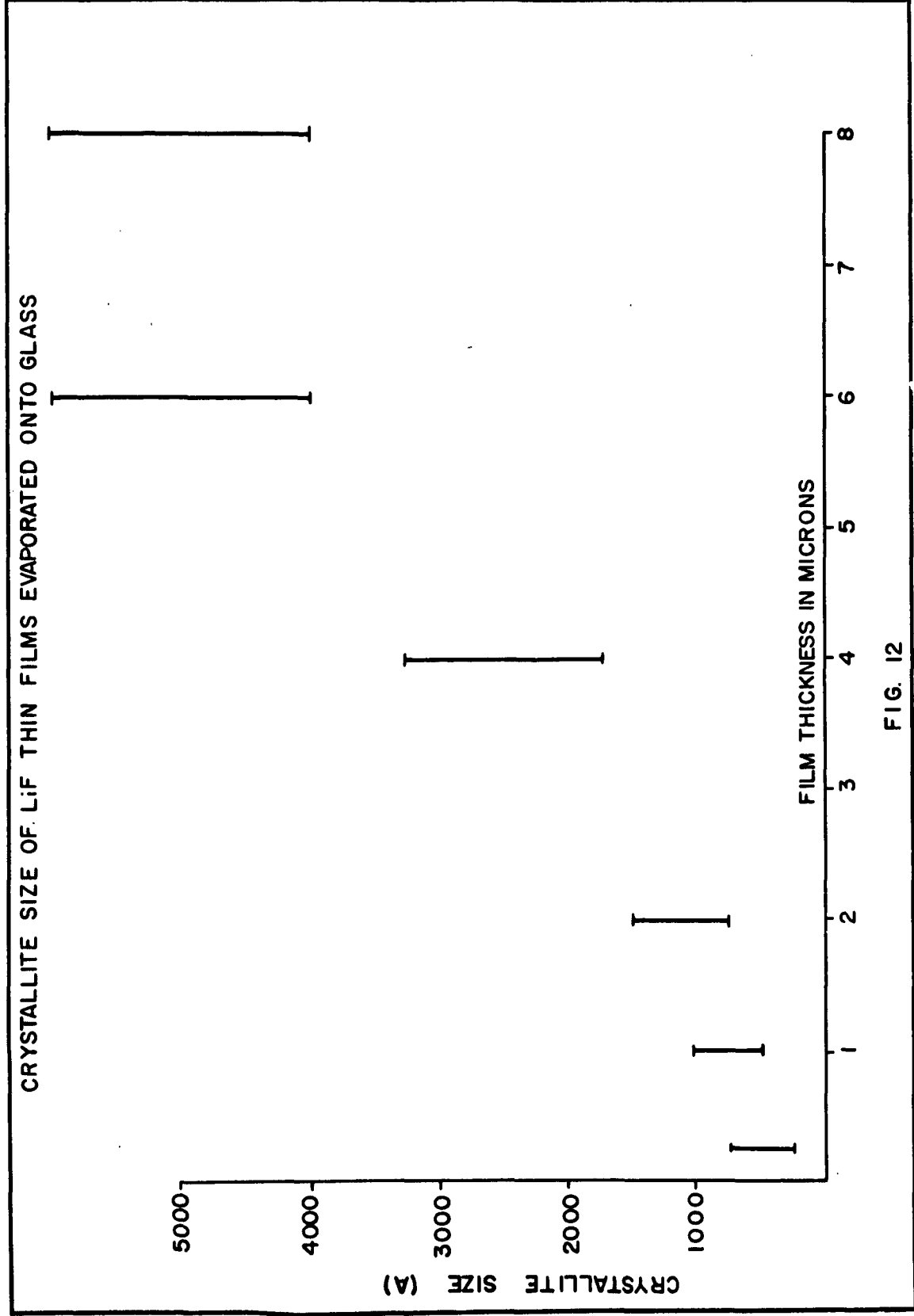


FIG. 12

CORRECTED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

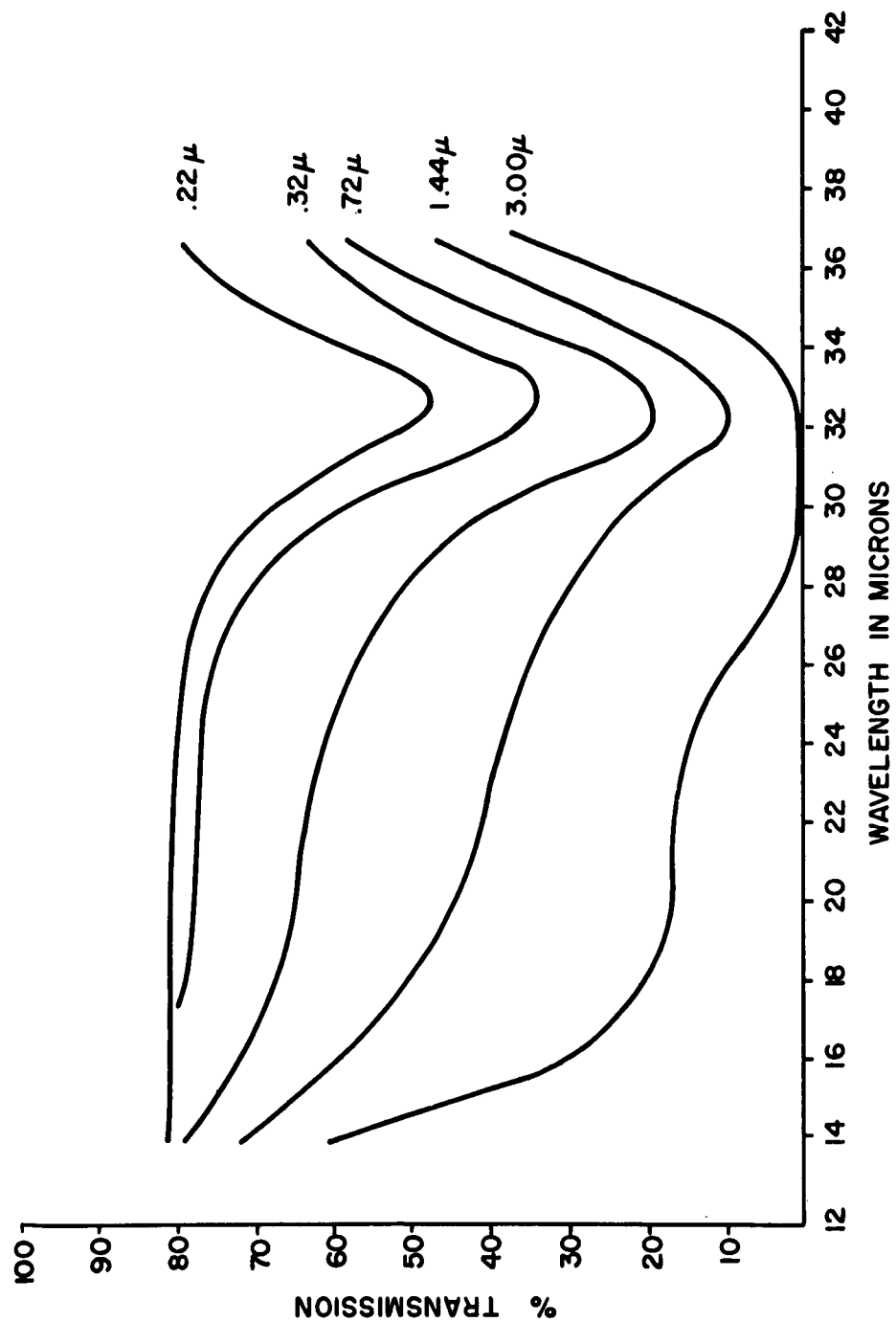


FIG. 13

CALCULATED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

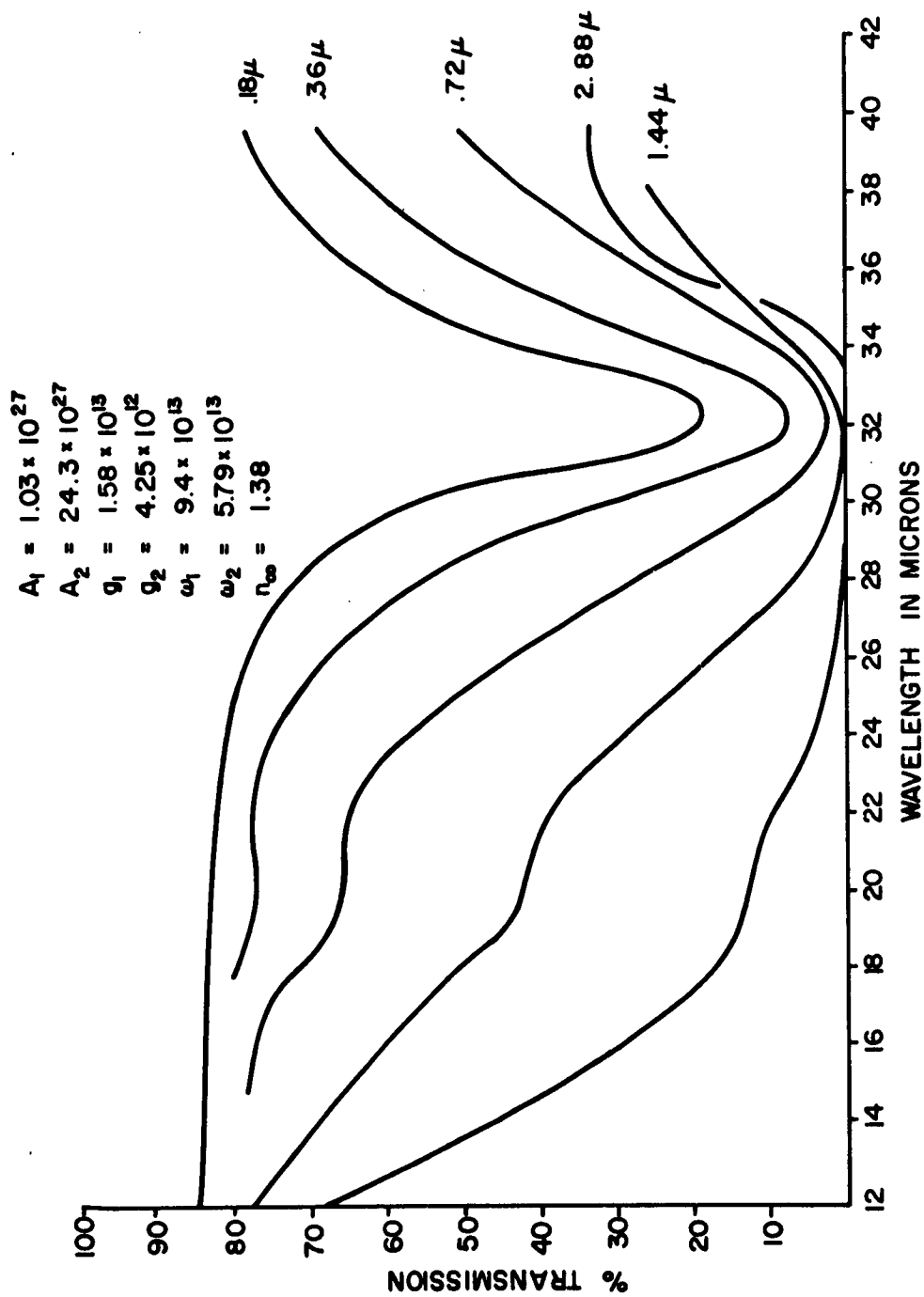
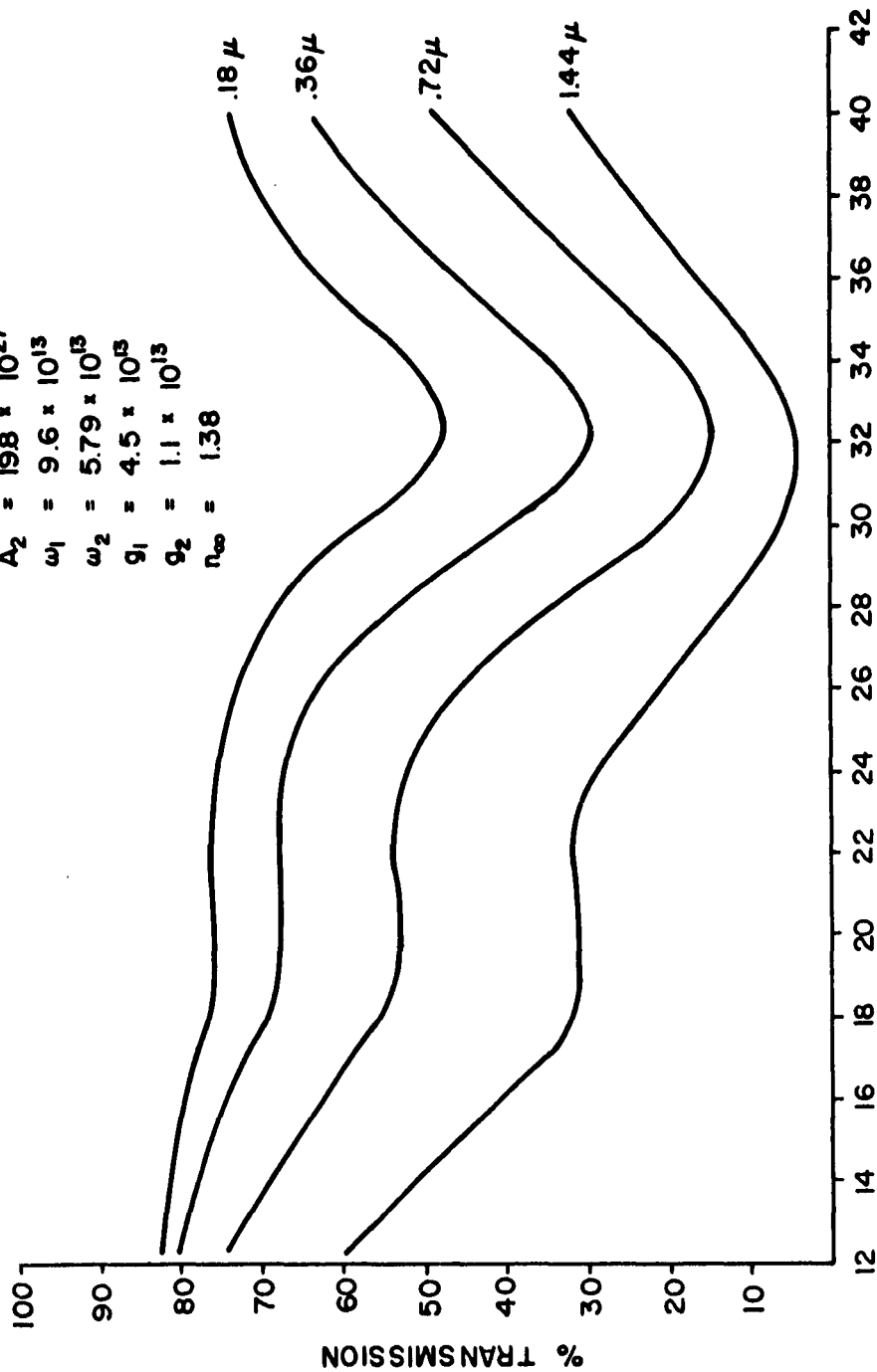


FIG. 14

CALCULATED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

$A_1 = 10.6 \times 10^{27}$
 $A_2 = 198 \times 10^{27}$
 $\omega_1 = 9.6 \times 10^{13}$
 $\omega_2 = 5.79 \times 10^{13}$
 $g_1 = 4.5 \times 10^{13}$
 $g_2 = 1.1 \times 10^{13}$
 $n_{\infty} = 1.38$



WAVELENGTH IN MICRONS
FIG. 15

TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

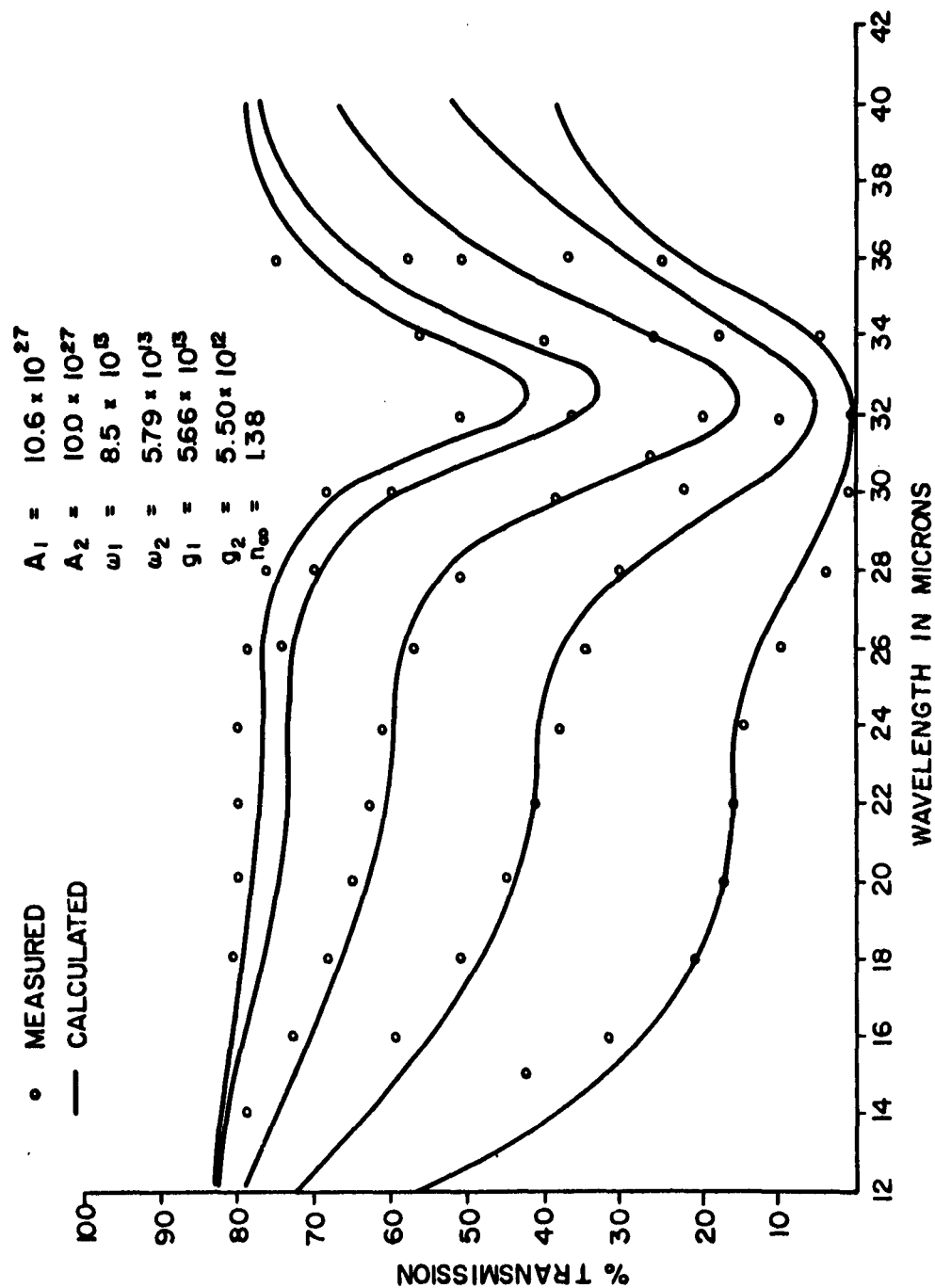


FIG. 16

RESTSTRAHLEN OF A LiF FILM EVAPORATED ONTO GLASS AT 35°C

THICKNESS— 6μ

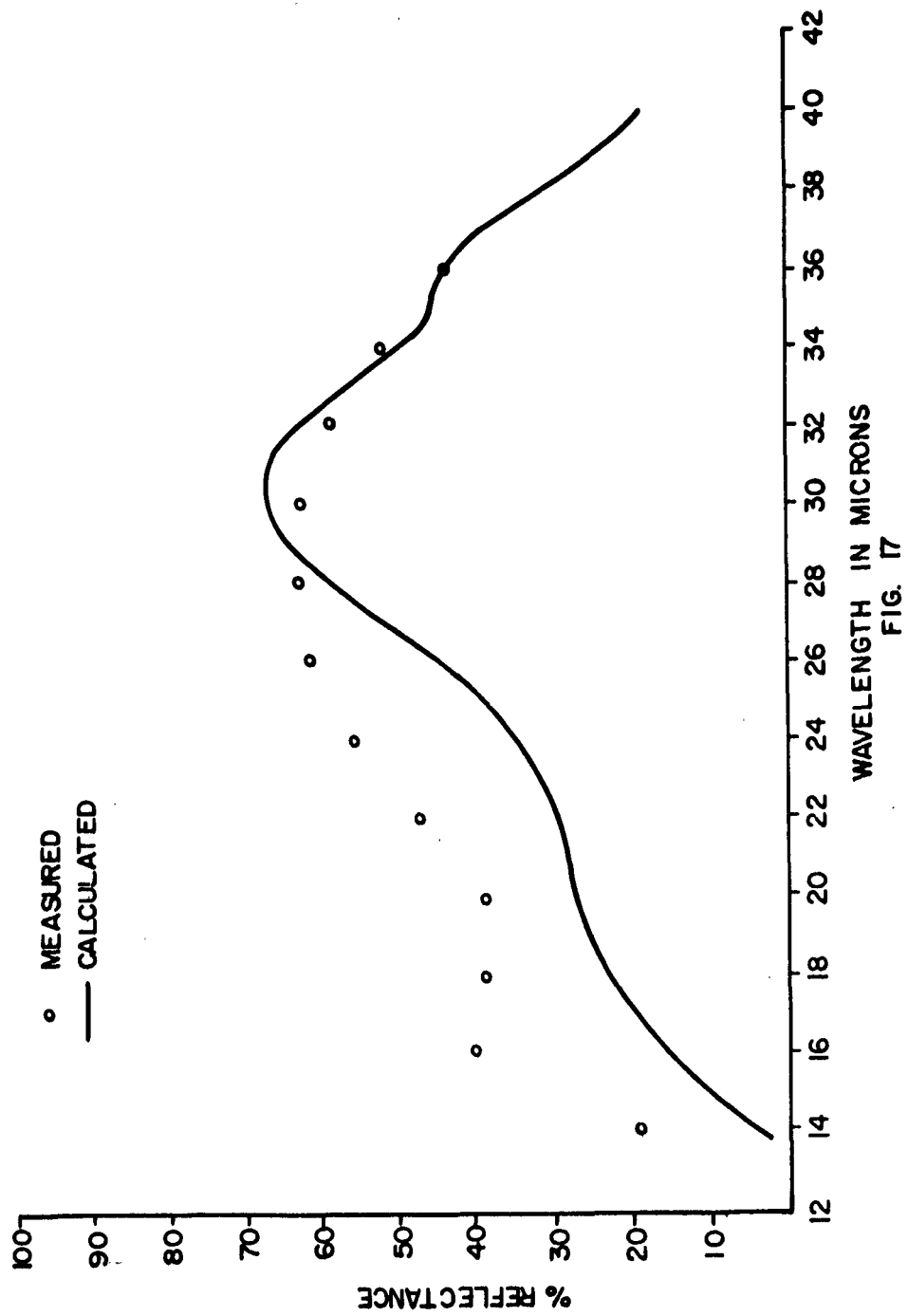


FIG. 17