NBS TECHNICAL NOTE 529

Determination of Oxygen Concentration in Silicon and Germanium by Infrared Absorption

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Infrared absorption measurements were made at room temperature, 80 K, and 20 K to determine the absorption coefficient of oxygen in silicon and germanium single crystals. A study was done to compare the results of four experimental methods, which involved both absolute and difference procedures. Sources of error were identified, including that due to calculating the absorption coefficient with an approximate equation which neglects multiple internal reflections. Measurements made on the same specimen at several temperatures give additional data on the relation of oxygen concentration to absorption coefficient at low temperatures.

Key Words: absorption coefficient; infrared absorption; germanium; methods of measurement; oxygen in germanium; oxygen in silicon; silicon

1. INTRODUCTION

This report summarizes results on the oxygen concentration of silicon and germanium single crystals determined by infrared absorption measurements at room temperature, 80 K, and 20 K. An important part of the report is an experimental comparison of absorption measurements made by various methods on silicon slices. The procedures followed in making the absorption measurements were essentially the same as those given in various ASTM documents [1].

The instrument used for most of the work was a Perkin-Elmer Model 337[*] double beam, infrared grating spectophotometer, linear in wavelength with adjustable slit width. A scale expansion accessory added to this instrument was available for most of the measurements. Also a slower scan motor (72 min to cover the range 7.5 to 25 μm) was installed for recording narrow absorption bands. Occasionally spectra were run on other instruments at NBS for comparison with those obtained on this spectrophotometer.

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[*] The commercial instrument is identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.
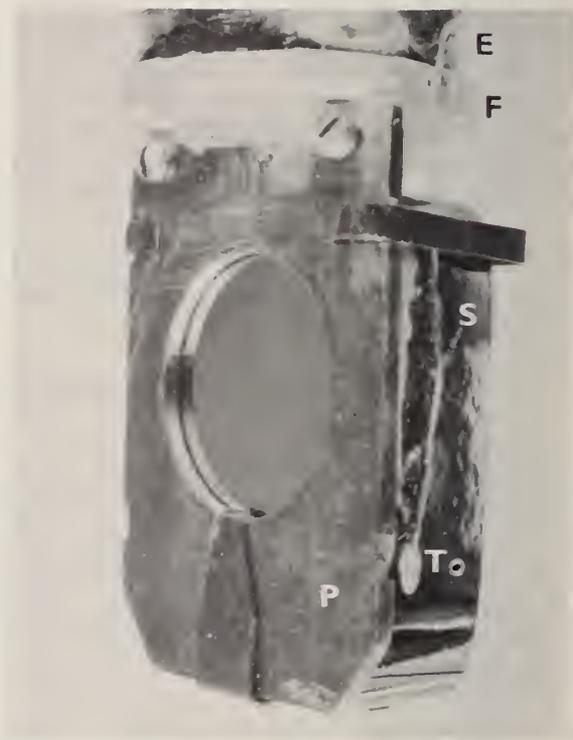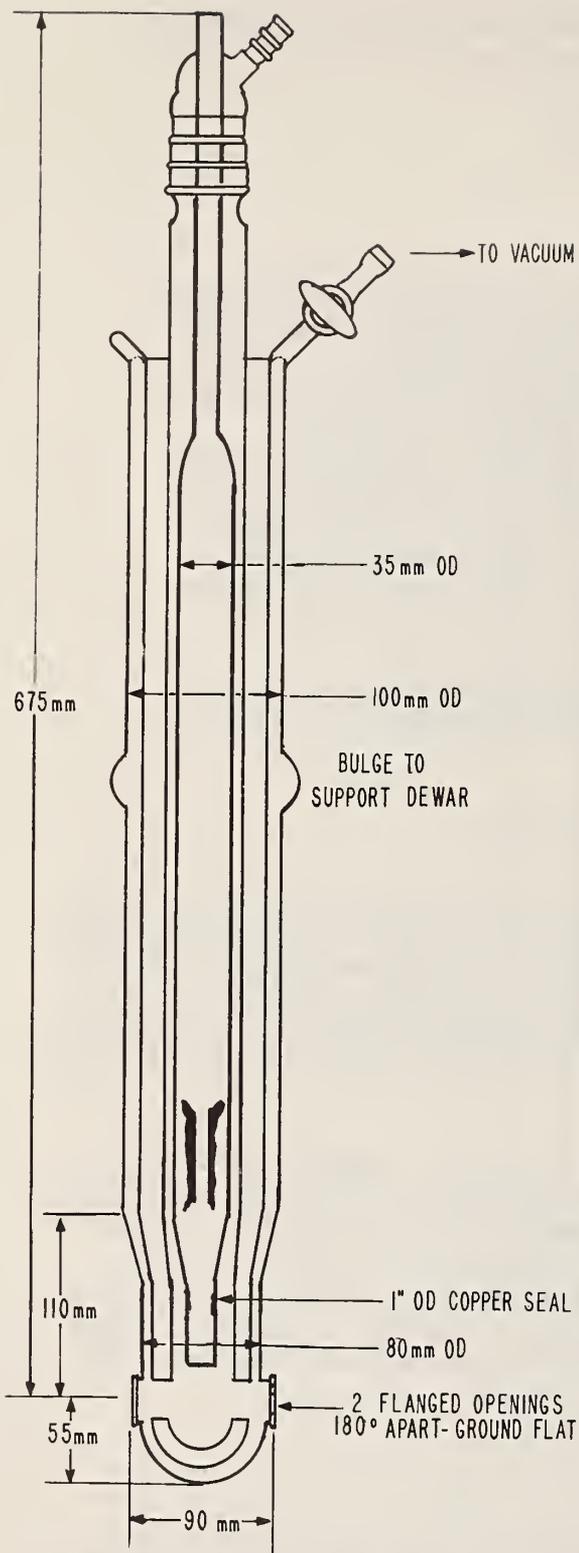
Figure 1. Dewar system used in sample beam of spectrophotometer. A photograph of the germanium specimen (S) mounted on a copper plate (P) attached to a flange (F) at the end (E) of the inner flask is shown in the inset. A thermocouple (T) is bonded to the side of the specimen.
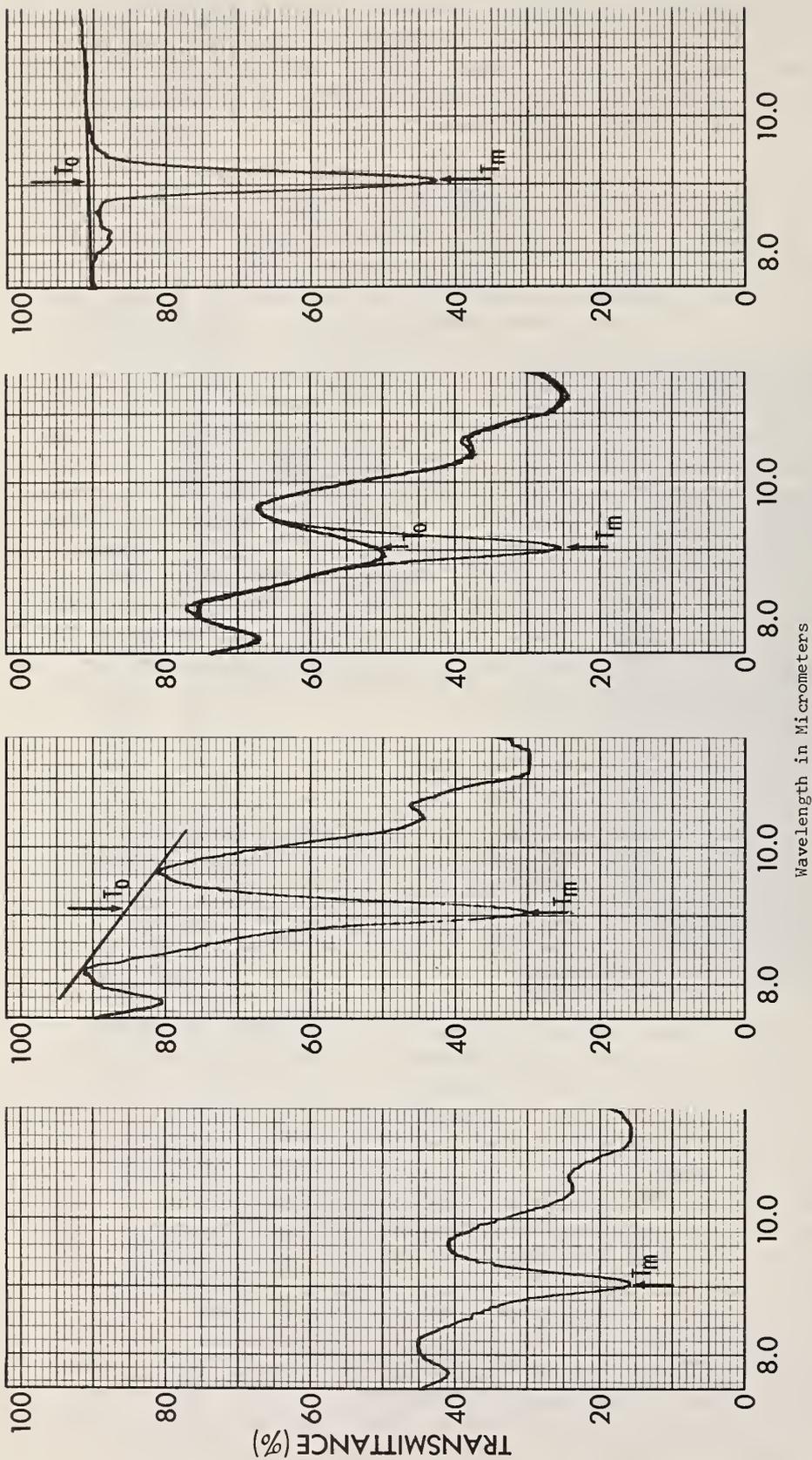
The absorption coefficient of oxygen increases with a decrease in temperature, so smaller concentrations of the impurity can be detected when the specimens are cooled. Double Dewar flasks were used to cool both the sample and reference specimens to temperatures of 80 K (liquid nitrogen) and 20 K (liquid helium in the inner flask).

The Dewar system for the sample beam shown in Fig. 1 is patterned after an optical cell designed by H. N. Hersh [2]. The Dewar system for the reference beam was similar but smaller in diameter to fit the available space in the spectrophotometer. Potassium bromide windows, 5-mm thick, were secured to the flanged openings with a varnish which provided the necessary vacuum seal. The specimens were mounted on copper plates with the aid of spring clips and conductive silver paste. This assured good thermal contact in order to dissipate heat from the specimen due to the incident radiation and the room temperature environment. As shown in the inset in Fig. 1, the plate was fastened to a flange soldered onto the copper seal at the end of the inner flask. The alignment was such that the hole in the plate through which the radiation passed was in the center of the Dewar windows. It was found that if the flask were positioned so that the copper plate faced the incoming radiation, then lower temperatures were reached than when the specimen faced the incident beam. This was attributed to the more direct path provided by the copper plate in conducting heat to the liquid helium. A thermocouple was glued to the side of the specimen (silver paste was used at the junction for better thermal contact) and the leads emerged from the Dewar system through the joint at the top of the inner flask.

2. EXPERIMENTAL PROCEDURES

There are several procedures by which the absorption coefficient due to an impurity in a crystal can be determined. All of the four methods investigated in this study should yield the same value for the absorption coefficient if the measurements are carefully done, the instrument is functioning properly, the correct equation is used, and the proper correction is made for lattice absorption.

The *absolute transmittance method* follows the procedure given in ASTM Method F45-64T [1]. The spectrophotometer is initially adjusted so that 100 percent transmittance is read with air in both beams and 0 percent is recorded with the sample beam blocked. Then the specimen, with polished, parallel faces, is placed in the sample beam and the spectrum recorded. An example is shown in Fig. 2a. The minimum percent transmittance T_m is noted for the 9-µm band and the absorption coefficient is determined by computations involving the transmission equation which is discussed in Section 3. For all but the most accurate work, a graph in the ASTM method can be used in lieu of the computations. The oxygen concentration is obtained from a calibration curve in the document. This procedure has the disadvantage that the absolute transmittance is used which requires correct 0 and 100 percent transmittance readings and necessitates good preparation of the specimen surfaces to keep scattered light to a minimum. Any surface films which affect the reflectivity will introduce errors. Also the specimen resistivity must be greater than

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Figure 2. These spectra illustrate the four methods used for determining the absorption coefficient of the 9-μm oxygen band in silicon. (a) Absolute transmittance recorded following procedure in ASTM Method F45-64T. (b) Relative transmittance recorded with air in the reference beam. Shown are the T_m and T_o used to calculate the absorption coefficient. (c) Relative transmittance traces for the single-beam difference method. An oxygen-free slice of the same thickness as the test specimen is run in the sample beam to obtain T_o. (d) Double-beam difference recording with an oxygen-free slice in the reference beam. The sample specimen for all of the spectra was a 5-mm thick slice from crystal L42Mx. The reference slice was from crystal 10190-4.

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1 Ω-cm; otherwise free carrier absorption will reduce the transmittance.

In the *air reference method*, the spectrum is also obtained with air in the reference beam of the spectrophotometer and then a straight baseline is drawn tangent to the peaks in transmittance on each side of the 9-μm absorption. In the example shown in Fig. 2b an attenuator was used in the reference beam to move the trace higher on the transmittance scale and thereby magnify the recording. The total absorption coefficient is calculated from the equation

$$T_m = T_o e^{-\alpha' x}$$ (1)

where

T_m = transmittance minimum for the impurity absorption peak,

T_o = baseline transmittance measured at the same wavelength as T_m,

α' = absorption coefficient, and

x = thickness of slice.

To obtain the absorption coefficient due to oxygen, a lattice contribution is subtracted from the total coefficient.

In the *single-beam difference method* (or reference standard method [3]) the test specimen and an oxygen-free crystal of the same thickness and surface finish are consecutively recorded on the same paper as shown in Fig. 2c. In Eq. (1), which is used for the calculations, T_m is the relative transmittance of the specimen at the impurity absorption peak and T_o is the transmittance of the oxygen-free reference slice at the same wavelength. The absorption coefficient α' is that due to oxygen only as using a reference crystal to obtain T_o eliminates the lattice absorption.

In the *double-beam difference procedure*, the spectrum is obtained with the test specimen in the sample beam and an oxygen-free slice of the same thickness in the reference beam. As illustrated by Fig. 2d, this method cancels out the lattice absorption. The baseline T_o is drawn as a straight line coincident with the transmittance trace on both sides of the absorption band. The flat baseline allows the trace to be made near the top of the transmittance scale, thereby giving a peak size which is larger than that obtainable by the other methods. Differences in free carrier absorption between the two slices will give an irregular or sloping baseline, but will have little effect on the impurity peak. Equation (1) is used to find the absorption coefficient due to oxygen. This difference procedure is generally the most accurate method, especially for small impurity concentrations, and may be the only one with the required sensitivity.

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Table 1. Results of measurements of the absorption coefficient of oxygen in silicon specimens by different methods

Crystal number	Specimen thickness	Absolute		Air reference			Single beam difference			Double beam difference		
		α	Std. dev.	$\alpha\acute{}^{a}$	Std. dev.	α^{b}	$\alpha\acute{}$	Std. dev.	α	$\alpha\acute{}$	Std. dev.	α
	cm	cm^{-1}		cm^{-1}		cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}		cm^{-1}
R818A	0.1036	2.03	0.08	2.21	0.04	2.22	2.38	0.03	2.10	2.69	0.06	2.39
	.201	2.08	.16	1.99	.05	2.09	2.12	.02	1.94	2.44	.12	2.24
	.500	2.38	.15	2.09	.09	2.31	2.29	.09	2.22	2.39	.07	2.32
L42Mx	.1037	1.24	.03	1.33	.03	1.43	1.45	.06	1.27	1.63	.03	1.43
	.201	1.35	.19	1.29	.04	1.44	1.41	.03	1.27	1.61	.11	1.46
	.500	1.39	.04	1.16	.02	1.40	1.35	.02	1.29	1.46	.04	1.40
1105	.177	1.21	.07	1.15	.05	1.30	1.23	.01	1.10	1.47	.05	1.32
1174	.201	1.15	.10	1.12	.07	1.28	1.31	.06	1.18	1.40	.04	1.26
602826	.185	3.65	.12	3.42	.16	3.43	3.60	.14	3.33	3.96	.03	3.68

[a] $\alpha\acute{}$ is the oxygen absorption coefficient calculated from the approximate equation $T_m = T_o e^{-\alpha\acute{} x}$.

[b] α is the oxygen absorption coefficient calculated using the complete transmission equation and includes corrections discussed in the text.

Table 2. Ratio of oxygen absorption coefficient at about 80 K to that at room temperature and oxygen concentration for silicon specimens

Specimen	Temperature	α_{80}	Temperature	α_{300}	α_{80}/α_{300}	Oxygen[a]
	K	cm^{-1}	K	cm^{-1}		atoms/cm^3
21-157-4-2	79	0.806	308	0.383	2.1	1.84×10^{17}
1174	80	3.03	308	1.26	2.4	6.05
reference [7][b]	78	3.4	297	1.8	1.9[c]	8.6
reference [4][d]	90	4.4	room	2.6	1.7	12.5

[a] Calibration equation: oxygen atoms/cm^3 = $4.8 \times 10^{17} \alpha_{300}$.

[b] Background absorption was estimated.

[c] Ratio 2.1 when slit width correction applied.

[d] Slit width not given.

3. COMPARISON OF METHODS FOR SILICON

Absorption measurements were made on several silicon specimens using each of the four methods given in Section 2. The results are given in Table 1. Each value listed is the average of about five recordings of the absorption band and an estimated standard deviation of the mean was calculated from the individual measurements. Also listed are the values after corrections were made for the known errors in the last three methods. Two corrections are necessary. The first involves the error introduced when the approximate equation, Eq. (1), which neglects multiple internal reflections, is used instead of the more complete equation

$$I = \frac{I_i \, (1-R)^2 \, e^{-\alpha x}}{1-R^2 e^{-2\alpha x}} \tag{2}$$

where
I = transmitted intensity measured at wavelength of impurity absorption peak,
I_i = radiation intensity on specimen at normal incidence,
R = reflectivity of a single air-crystal interface,
α = absorption coefficient, and
x = thickness of slice.

The calculations relating the absorption coefficient α determined by Eq. (2) with the α' of Eq. (1) for both air reference and difference methods are outlined in the appendixes. To determine when Eq. (1) can be used without appreciable error (10 %), calculations were made for a range of oxygen absorption coefficients and specimen thicknesses using constants appropriate for germanium and silicon. Graphs of the results are given in the appendixes.

The second correction applies only to the air reference method and involves the baseline intensity which is used in the approximate equation. The baseline tangent to the peaks in transmittance on each side of the oxygen band does not place all of the lattice absorption (0.8 cm^{-1}) under the baseline, but only that amount in the lattice peak. From the work of Kaiser, Keck, and Lange [4], it is evident that the excluded lattice absorption is about half of the total value. Thus it would be more appropriate to subtract 0.4 cm^{-1}, instead of 0.8 cm^{-1}, when determining the oxygen absorption coefficient by the air reference method. Consequently 0.4 cm^{-1} was added to each of the absorption coefficients in the corrected column for the air reference measurements.

The corrected absorption coefficients as determined by the four methods (Table 1) are in reasonable agreement. If 0.4 cm^{-1} had not been added to each of the air reference values, all of these would be much smaller than those obtained from the other methods. Other trends are: (1) The double-beam difference method always gives a larger coefficient than the single-beam difference method, and (2) for the absolute transmittance method the absorption coefficient varies systematically with specimen thickness, with thicker specimens in better agreement with the

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other methods. The latter trend is not unexpected as the various errors (such as 0 and 100 percent transmittance settings and surface preparation) are relatively more important for a thin specimen than for a thick one.

Another source of error in the measurements was the non-linearity of the spectrophotometer as a function of baseline transmittance. This error is most readily observed in the double-beam difference method by running the specimens at a high transmittance baseline and then repeating the scan at a lower transmittance baseline (achieved by adjusting the 100 percent control). Consistently, it was found that the absorption coefficient determined from a baseline of 70 to 80 percent transmittance was several percent smaller than that claculated from a 90 to 100 percent baseline. This result may not be typical as the effect was somewhat smaller on another instrument of similar design.

Another factor which may affect the results is the spectral slit width of the spectrophotometer and its relation to the full width at half maximum intensity (FWHM) of the impurity peak. The spectral slit width is the mechanical width of either the exit or the entrance slit, whichever is the larger, divided by the linear dispersion in the exit slit plane. The spectral slit width must be narrow enough so that the full peak height will be reproduced. The oxygen absorption band in silicon has a Gaussian profile at room temperature with a wide FWHM so that the slit setting of the instrument is not critical. The FWHM observed in this work was 35 cm^{-1} and values quoted in the literature are 30 cm^{-1} [5] and 32 cm^{-1} [6]. The FWHM determined from the spectra of Hrostowski and Kaiser [7] was about 32 cm^{-1}. The appropriate ASTM document gives 32 cm^{-1}. At 80 K the oxygen band is narrow so correspondingly narrow instrument slit widths must be used. The FWHM at 80 K found in this work was 20 cm^{-1} and values from the literature are also about 20 cm^{-1} [4,7]. The ASTM value for 80 K is likewise 20 cm^{-1}.

When recording sharp absorption bands with narrow slit widths, it is important to scan the wavelength range of interest at a slow speed. Otherwise the peak height will be attenuated or, with a fast pen response, overshoot may occur due to the rapid change of absorption. A slow scan speed will improve the signal to noise ratio as the pen response can be reduced without loss of detail. The reproducibility of the peak shape is a useful criterion in determining the quality of the recording. When the peak is narrow, abscissa expansion is necessary to determine its shape and FWHM. The expansion was achieved by using an external recorder in conjunction with the 72 min scan speed of the spectrophotometer. Ordinate expansion was also used when the peak height was small.

4. OXYGEN CONCENTRATION AND TEMPERATURE DEPENDENCE OF ABSORPTION COEFFICIENT FOR SILICON

Recent measurements [8] on the relation between absorption coefficient and oxygen concentration are in disagreement with the earlier work of Kaiser and Keck [9], which serves as the calibration for ASTM method

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F-45. The new equation relating oxygen content to the absorption coefficient at 9 μm [oxygen atoms/cm^3 = 4.8 × 10^{17} α (cm^{-1})] gives about twice the oxygen that is obtained by use of Kaiser and Keck's results. Infrared absorption measurements and the lithium precipitation method [10] give the same amount of oxygen in silicon crystals if the new calibration is used for the infrared work. Also the oxygen content in silicon as determined by [3]He activitation [11] was about twice that found by infrared absorption. The calibration equation used for the absorption analysis was not given, but the Kaiser and Keck relation was probably used as it has been the customary one. The use of the new calibration would bring the oxygen content as determined by absorption into close agreement with that found by [3]He activation.

As mentioned in the introduction, the height of the absorption peak increases with a decrease in temperature. At room temperature the absorption appears as a single peak, but when the specimen is cooled two peaks emerge which are well resolved at 80 K [7]. At 20 K, the peak which was the stronger of the two at 80 K is now the weaker one. The stronger absorption peak at 18 K has a coefficient about three times as large as that of the broad peak at 297 K [7]. On the one specimen measured at 20 K in the present work, a value of about 5 was found for the ratio α_{20}/α_{300}. Pajot [5] measured specimens cooled to 8 K using a narrow spectral slit width (0.32 cm^{-1}) and found that α_8/α_{300} was about 25. Since the absorption coefficient is this strong at liquid helium temperatures, it is possible to determine oxygen concentrations down to about 1 × 10^{14} atoms/cm^3. The disadvantages of the procedure are the narrow slit width required to obtain the full peak height and the low temperature which must be consistently achieved.

Measurements at 80 K are of special interest as the ASTM Method F121-70T includes a calibration for this temperature. Table 2 lists absorption coefficients obtained at temperatures near 80 K and 300 K and the ratio calculated from the coefficients. Also included is the oxygen concentration for each specimen based on the coefficient at 300 K. For the literature references the data were taken from the published graphs, and the background absorption for an oxygen-free slice was subtracted to get only the absorption coefficient due to oxygen. The double-beam difference method was used for the present measurements at room temperature and at 80 K. A gold-cobalt versus chromel thermocouple was used to determine the temperature. The value of 308 K given for nominal room temperature measurements was the temperature obtained by attaching a thermocouple directly to one of the specimens. Thus the heating of the specimens by the infrared beam can give some error if the calibration is based on results at 300 K. The work of Hrostowski and Kaiser [7] can be extrapolated above 300 K to get an approximate idea of the change in absorption coefficient with temperature. It is fortunate that α varies slowly with temperature so that heating of the specimens will not be a major source of error.

Hrostowski and Kaiser state that their absorption coefficients have a maximum error of 10 percent in regions of strong absorption because of the slit widths which were used in recording the narrow bands. Since at

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room temperature the band is wide, the error occurs only for 80 K meas-
urements and a correction of 10 percent in the ratio α_{80}/α_{300} of Table 2
increases it to 2.1. The slit width used in the present work was suffi-
ciently narrow so that any corrections would be only a few percent. The
absorption coefficient calculations were made with Eq. (2) using 0.4 cm^{-1}
for the lattice absorption coefficient at 80 K and 0.2964 for the reflec-
tivity.

On the basis of this work and various ASTM round robins, it appears
that ±20 percent is a realistic figure to expect for the multi-laboratory
precision for determination of oxygen in silicon by infrared absorption.

5. MEASUREMENTS ON GERMANIUM

Procedures similar to those described for silicon may be used for
measurements on germanium. There is some disagreement on the calibration
equation relating the absorption coefficient of the 11.7-μm band to the
interstitial oxygen concentration. Kaiser and Thurmond [12] used vacuum
fusion determinations made with an iron bath to calibrate their infrared
absorption measurements and found that oxygen atoms/cm^3 = 0.5 × 10^{17}
α (cm^{-1}). Millett, Wood, and Bew [13] repeated the work and obtained in-
consistent results with an iron bath. However, when they used a platinum
bath their data was consistent to about 20 percent of the total oxygen
content. The calibration found was that oxygen atoms/cm^3 = 1.25 × 10^{17} α
(cm^{-1}). This is the same factor that Bloem, Haas, and Penning [14] de-
rived, but this is coincidental, as they based their calculation on sili-
con data which is now considered inaccurate. Fox [15] determined the
oxygen content of germanium by the lithium precipitation technique and
compared the results with infrared absorption measurements on specimens
cooled to 20 K. The calibration obtained was that oxygen atoms/cm^3 = 3.1
× 10^{16} α (cm^{-1}). This is in good agreement with the results of Millett,
et al., as data on the variation of the absorption coefficient with temp-
erature show that the coefficient is about four times larger at 20 K than
at 300 K.

The free carrier absorption coefficient per unit carrier concentra-
tion is about ten times higher in p-type than in n-type germanium [16].
The absorption cross section in p-type material is 7 × 10^{-16} cm^2 at 11.7
μm for both 300 and 80 K [16-18], and the absorption coefficient is the
product of the cross section and the carrier concentration. The data
from measurements on many specimens at room temperature, 80 K, and 20 K
were analyzed to compare the expected values for the background absorp-
tion coefficient with the experimental ones. The coefficients varied
from 0.07 to 0.15 cm^{-1}, independent of temperature, for p-type specimens
with carrier concentrations in the range 4 × 10^{13} to 2 × 10^{14} cm^{-3}. The
correction for multiple reflections is fairly insensitive to the value
used for the background absorption coefficient, so 0.1 cm^{-1} was used for
the specimens included in this report as they all had carrier concentra-
tions below 2 × 10^{14} cm^{-3}. This is also the value used by Kaiser and
Thurmond [12] for room temperature measurements on a specimen with low
carrier density.

Table 3. Absorption coefficient and FWHM as a function of temperature for the 11.7 μm oxygen band in germanium specimen NBS-91 (thickness 1.19 cm)

Temp.	Spectral Slit width	α'	Std. dev.	R	α	FWHM	Peak area ($\alpha \cdot$ FWHM)
K	cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}	cm^{-2}
305	3.5	0.0081	0.0006	0.360	0.0066	4.7	0.031
229	3.5	.012	.002	.358	.0097	4.7	.046
153	3.5	.017	.002	.356	.014	3.6	.050
81	3.5	.027	.002	.354	.022	3.5	.077
81	2.5	.028	.005	.354	.023	2.8	.064
23	3.5	.030	.002	.352	.025	2.8	.070
23	2.5	.039	.003	.352	.032	2.6	.083

Table 3 lists measurements at several temperatures of the absorption coefficient and FWHM of the oxygen band in specimen NBS-91. The double-beam difference method was used and the calculations were corrected to include the effects of multiple internal reflections. The absorption coefficient obtained at 23 K with the narrow slit width is significantly larger than the one found using the wider slit. The area under the absorption band increases with a decrease in temperature. The FWHM at room temperature may be concentration dependent as measurements on several specimens indicated that the FWHM increased as the oxygen concentration increased. The literature references give values for FWHM of 5 cm^{-1} [14] and 6 cm^{-1} [19], whereas the appropriate ASTM document lists 8 cm^{-1} [1]. Bloem, Haas, and Penning [14] give 3 cm^{-1} for the FWHM at 77 K, and a value of 2.8 cm^{-1} is obtained from the work of Kaiser [19]. At 5 K a value of 2.5 cm^{-1} is determined from spectra of Kaiser. All of the low temperature FWHM, including those in Table 3, may be slightly greater than the true ones because of the relatively wide slit widths used.

Table 4 gives the temperature variation of the absorption coefficient of the 11.7 μm oxygen band. Literature values, in addition to the data obtained in this work, are included. Room temperature was estimated as 305 K to include heating by the infrared beam. The low temperature values were calculated from thermocouple readings for each specimen. All measurements were made by the double-beam difference method and were

Table 4. Temperature dependence of the absorption coefficient of oxygen in germanium specimens

Specimen	Thickness	Room temperature		Liquid nitrogen		Liquid helium		$\frac{\alpha_{80}}{\alpha_{300}}$	$\frac{\alpha_{20}}{\alpha_{300}}$
		T	α	T	α	T	α		
	cm	K	cm^{-1}	K	cm^{-1}	K	cm^{-1}		
NBS-01	0.844	305	0.015	80	0.028	24	0.040	1.9	2.7
NBS-23	1.18	305	0.0095	79	0.025	12	0.033	2.6	3.5
NBS-24	1.19	305	0.0071	78	0.018	12	0.025	2.5	3.5
NBS-91	1.19	305	0.0066	81	0.023	23	0.032	3.5	4.8
NBS-101	1.09	305	0.11	81	0.26	47	0.33	2.4	3.0
Reference[14]		300	0.38	77	1.0			2.6	
Reference[19]		300	5.9	77	12.9	5	14.2	2.2	2.4

Table 5. Oxygen content of germanium crystals as determined by infrared absorption measurements on specimens at room temperature and at about 20 K

Crystal number	300 K - difference method			20 K - air reference method			20 K - difference method		
	α	Std. dev.	Oxygen	α	Std. dev.	Oxygen	α	Std. dev.	Oxygen
	cm^{-1}		atoms/cm^3	cm^{-1}		atoms/cm^3	cm^{-1}		atoms/cm^3
NBS-01	0.015	0.002	19×10^{14}	0.058	0.006	18×10^{14}	0.040	.0.004	12×10^{14}
NBS-02							.0083	.0018	2.6
NBS-23	.0095	.0017					.033	.003	10
NBS-24	.0071	.0009	8.9	.036	.004	11	.025	.002	7.7
NBS-71							.0045	.0007	1.4
NBS-91	.0066	.0005	8.3	.033	.004	10	.032	.002	9.9
NBS-101	.113	.003	141	.35	.01	108	.33	.01	100
NBS-613							.0071	.0009	2.2

corrected for multiple internal reflections. The ratios for specimen NBS-91 are noticeably larger than those for the other specimens, but no explanation can be given.

Table 5 lists the absorption coefficient and oxygen content of germanium crystals as determined from infrared absorption measurements by the double-beam difference method at about 300 K and by the difference and air reference methods at about 20 K. All of the absorption coefficients have been corrected for multiple internal reflections. Each reported value is the average of 5 to 10 recordings of the absorption band and an estimated standard deviation of the mean was calculated from the individual measurements. There is probably additional systematic error as evidenced by disagreements between the results of the air reference and difference methods on the same specimen at the same temperature. A flat baseline occurs in the difference measurements and this reduces the error involved in sketching the steep baseline corresponding to an oxygen-free crystal, which is required to analyze the data with air in the reference beam. The oxygen concentrations at 300 K were obtained using the calibration of Millet, et al. For 20 K measurements the work of Fox was used to relate oxygen content to absorption coefficient.

A minimum absorption coefficient of about 0.003 cm^{-1} can be detected in a 1-cm thick specimen using the double-beam difference method with ordinate scale expansion. Of course, the accuracy is poor for coefficients this small. At 20 K, an absorption coefficient of 0.003 cm^{-1} corresponds to an oxygen concentration of just under 1×10^{14} atoms/cm^3.

The oxygen content of most of the specimens listed in Table 5 has been determined by lithium precipitation and by lithium ion mobility. These results will be discussed and compared with the infrared absorption measurements in a forthcoming NBS Technical Note.

ACKNOWLEDGEMENTS

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CALCULATION AND GRAPHS RELATING THE IMPURITY ABSORPTION COEFFICIENT OBTAINED BY THE APPROXI-
MATE EQUATION TO THAT FOUND FROM THE COMPLETE EQUATION FOR THE DIFFERENCE METHODS

The impurity absorption coefficient is determined by calculations involving the ratio of
the transmittance at the impurity peak (T_m) to the transmittance at the same wavelength for
no impurity absorption (T_o). The intensity in the sample beam of the spectrophotometer at
the impurity peak is

$$I_s = \frac{KI_i(1-R)^2 e^{-\alpha_t x}}{1-R^2 e^{-2\alpha_t x}}$$

with the total absorption coefficient $\alpha_t = \alpha_i + \alpha_b$, where α_i is the impurity absorption co-
efficient and α_b is the background coefficient which includes lattice and free carrier ab-
sorption. The constnat K represents an attenuation of the sample beam which is achieved by
adjusting the 100 % control. The intensity in the reference beam which contains an impurity-
free specimen is

$$I_r = \frac{I_i(1-R)^2 e^{-\alpha_b x}}{1-R^2 e^{-2\alpha_b x}} \ .$$

The minimum transmittance at the impurity peak is

$$T_m = \frac{I_s}{I_r} = Ke^{-\alpha_i x} \ \frac{1-R^2 e^{-2\alpha_b x}}{1-R^2 e^{-2\alpha_t x}} \ .$$

The baseline transmittance is $T_o = \left. \frac{I_s}{I_r} \right|_{\alpha_i=0} = K \ .$

Thus $$\frac{T_m}{T_o} = e^{-\alpha_i x} \ \frac{1-R^2 e^{-2\alpha_b x}}{1-R^2 e^{-2\alpha_t x}} \ .$$

When the approximate equation is used, an α_i' is obtained from $T_m/T_o = e^{-\alpha_i' x} \ .$

Equating the above two equations, the solution obtained for α_i' in terms of α_i and the other
parameters is

$$\alpha_i' = \alpha_i + \frac{1}{x} \ \ln\left(\frac{1-R^2 e^{-2\alpha_t x}}{1-R^2 e^{-2\alpha_b x}}\right) .$$

In the limit of small $\alpha_i x$ the above equation can be written as

$$\left. \frac{\alpha_i' - \alpha_i}{\alpha_i} \right|_{\alpha_i x \to 0} = \frac{2R^2 e^{-2\alpha_b x}}{1-R^2 e^{-2\alpha_b x}} \ .$$

Thus the percent error is independent of α_i when α_i is small as clearly shown in the graphs
which follow. In the limit of small $(\alpha_i + \alpha_b) x$, the quantity $(\alpha_i' - \alpha_i)/\alpha_i$ approaches
$2R^2/(1-R^2)$, a limit dependent only on the reflectivity value. For semiconductors with a
high reflectivity, such as germanium, this factor is large and corrections are needed when
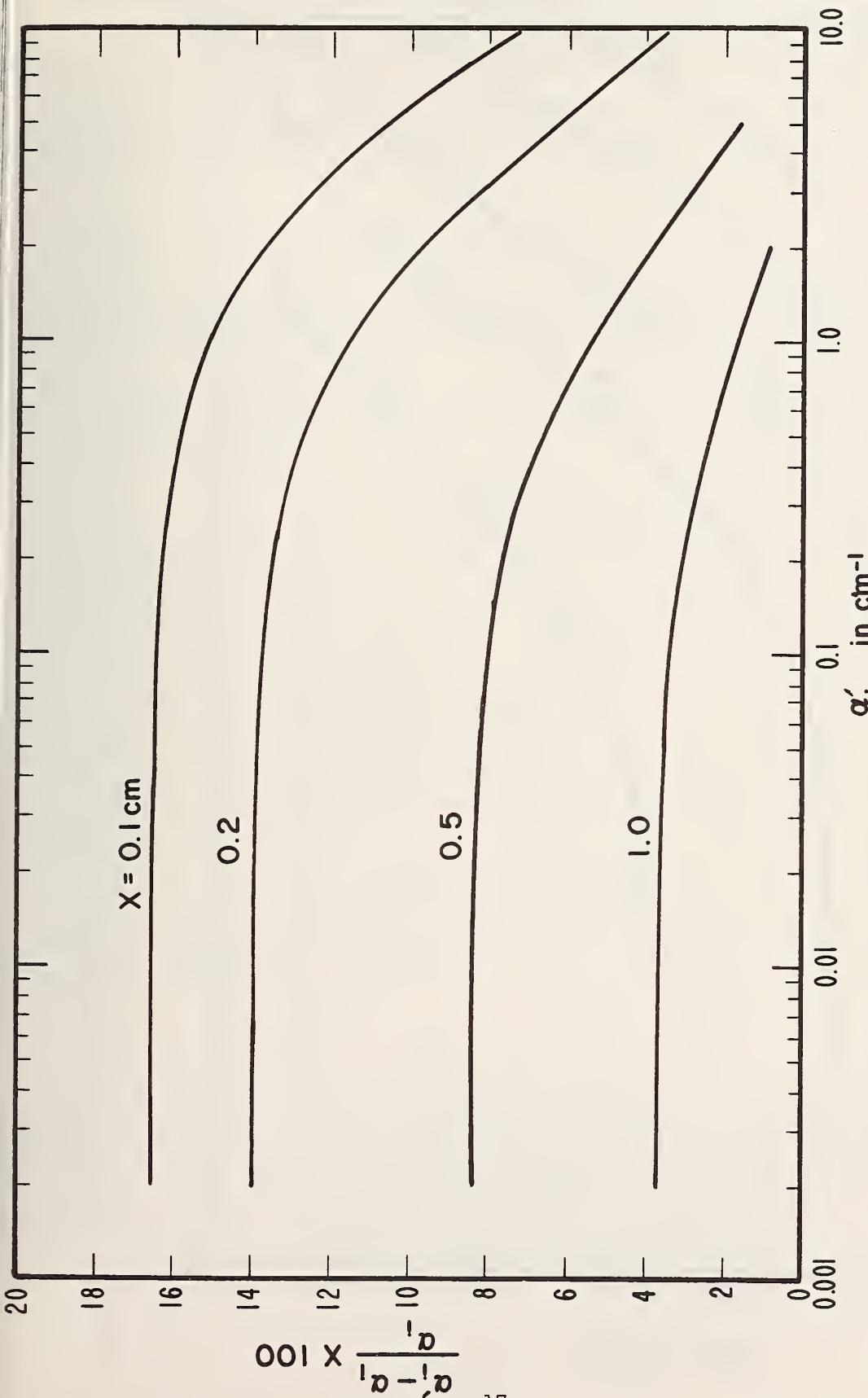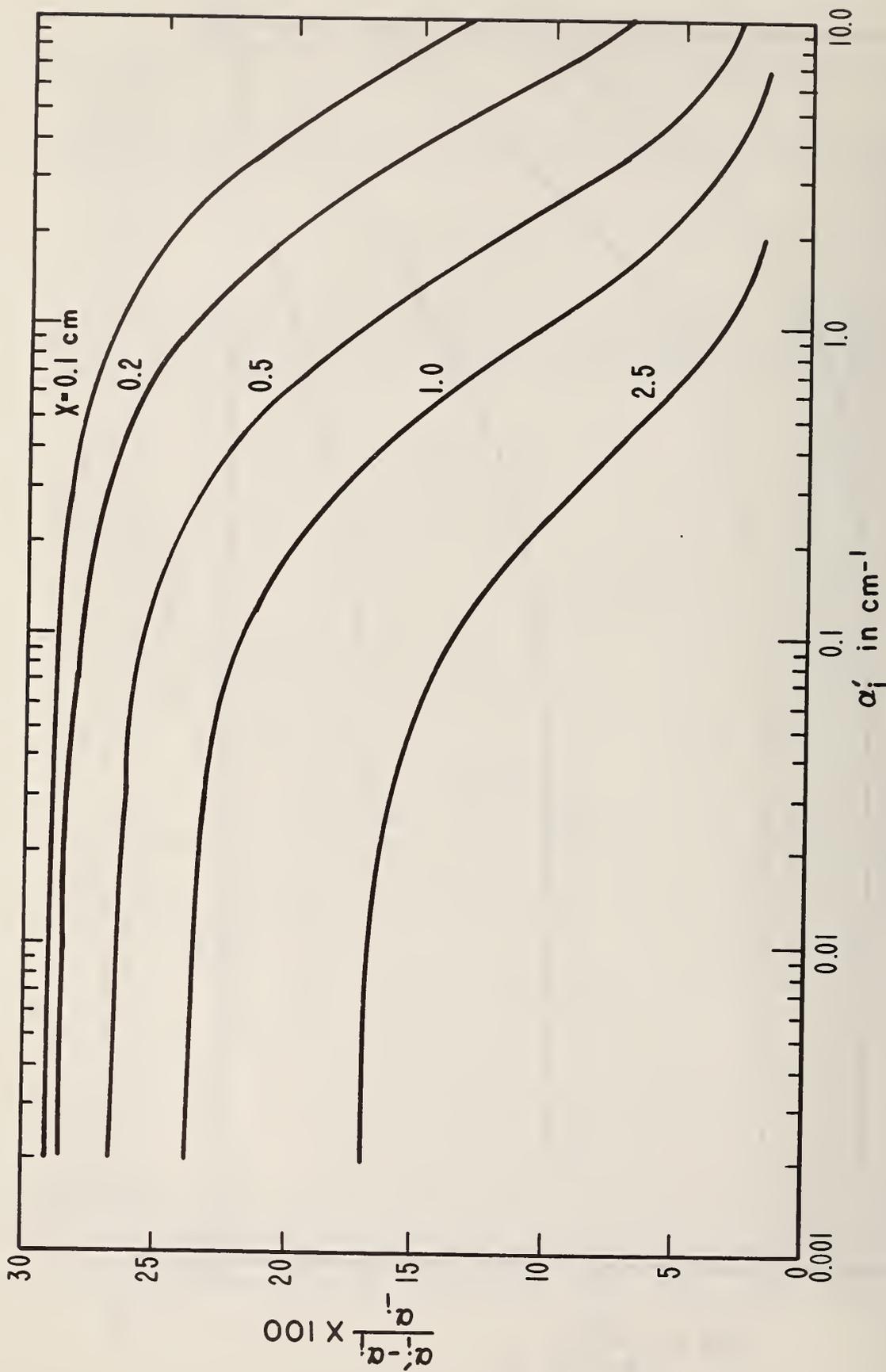the approximate equation is used for calculations.

Figure 3. Graph for the difference methods of the percent difference between the impurity absorption coefficient determined using the complete transmittance equation and that found from the approximate equation for several values of specimen thickness x. The constants used were $R = 0.2995$ and $\alpha_b = 0.8$ cm^{-1}, which are appropriate for the 9-μm oxygen band in silicon at 300 K.

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Figure 4. Graph for the difference methods of the percent difference between the impurity absorption coefficient determined using the complete transmittance equation and that found from the approximate equation for several values of specimen thickness x. The constants used were $R = 0.360$ and $\alpha_b = 0.1$ cm^{-1}, which are appropriate for the 11.7-μm oxygen band in germanium at 300 K.

CALCULATION AND GRAPH RELATING THE IMPURITY ABSORPTION COEFFICIENT OBTAINED BY THE APPROXI-
MATE EQUATION TO THAT FOUND FROM THE COMPLETE EQUATION FOR THE AIR REFERENCE METHOD

The impurity absorption coefficient is determined by calculations involving the ratio of
the transmittance at the impurity peak (T_m) to the transmittance at the same wavelength for
no specimen absorption (T_o). The intensity in the sample beam of the spectrophotometer at
the impurity peak is

$$I_s = \frac{I_i \ (1-R)^2 \ e^{-\alpha_t x}}{1-R^2 \ e^{-2\alpha_t x}}$$

with $\alpha_t = \alpha_i + \alpha_b$, where α_i is the impurity absorption coefficient and α_b is the background
coefficient which includes lattice and free carrier absorption. The intensity in the refer-
ence beam with only air is

$$I_r = K \ I_i$$

where the constant K represents at attenuator in the reference beam. The minimum transmitt-
ance at the impurity peak is

$$T_m = \frac{I_s}{I_r} = \frac{(1-R)^2 \ e^{-\alpha_t x}}{K \ (1-R^2 \ e^{-2\alpha_t x})} \ .$$

Assume that the baseline is drawn to coincide with the transmittance for no specimen absorp-
tion (only reflectivity losses); then

$$T_o = \frac{I_s}{I_r} \bigg|_{\alpha_t = 0} = \frac{(1-R)^2}{K \ (1-R^2)} \ .$$

Thus
$$\frac{T_m}{T_o} = e^{-\alpha_t x} \ \frac{(1-R^2)}{1-R^2 e^{-2\alpha_t x}} \ .$$

When the approximate equation is used, an α_t' is obtained from $T_m/T_o = e^{-\alpha_t' x}$.

Equating the above two equations, the solution obtained for α_t' in terms of α_t and the other
parameters is

$$\alpha_t' = \alpha_t + \frac{1}{x} \ \ln \left(\frac{1-R^2 \ e^{-2\alpha_t x}}{1-R^2} \right).$$

Using the relations that $\alpha_t' = \alpha_i' + \alpha_b$ and $\alpha_t = \alpha_i + \alpha_b$, it is possible to write the above
equation as

$$\frac{\alpha_i' - \alpha_i}{\alpha_i} = \frac{1}{\alpha_i x} \ \ln \left(\frac{1-R^2 e^{-2(\alpha_i + \alpha_b)x}}{1-R^2} \right).$$

It is clear from this equation and the graph on the next page that the approximate equation
should not be used unless the impurity absorption is larger than any competing background
absorption regardless of the value of the reflectivity. Providing there is no competing ab-
sorption ($\alpha_b = 0$), the approximate equation can be used with the air reference method when
$\alpha_i x$ is small, as the correction factor is simply $2R^2/(1-R^2)$, which is the limit found in the
same situation for the difference methods. It is well to remember that this factor is signi-
ficant when R is large. For silicon with R = 0.30, it is a 20 percent correction. In the
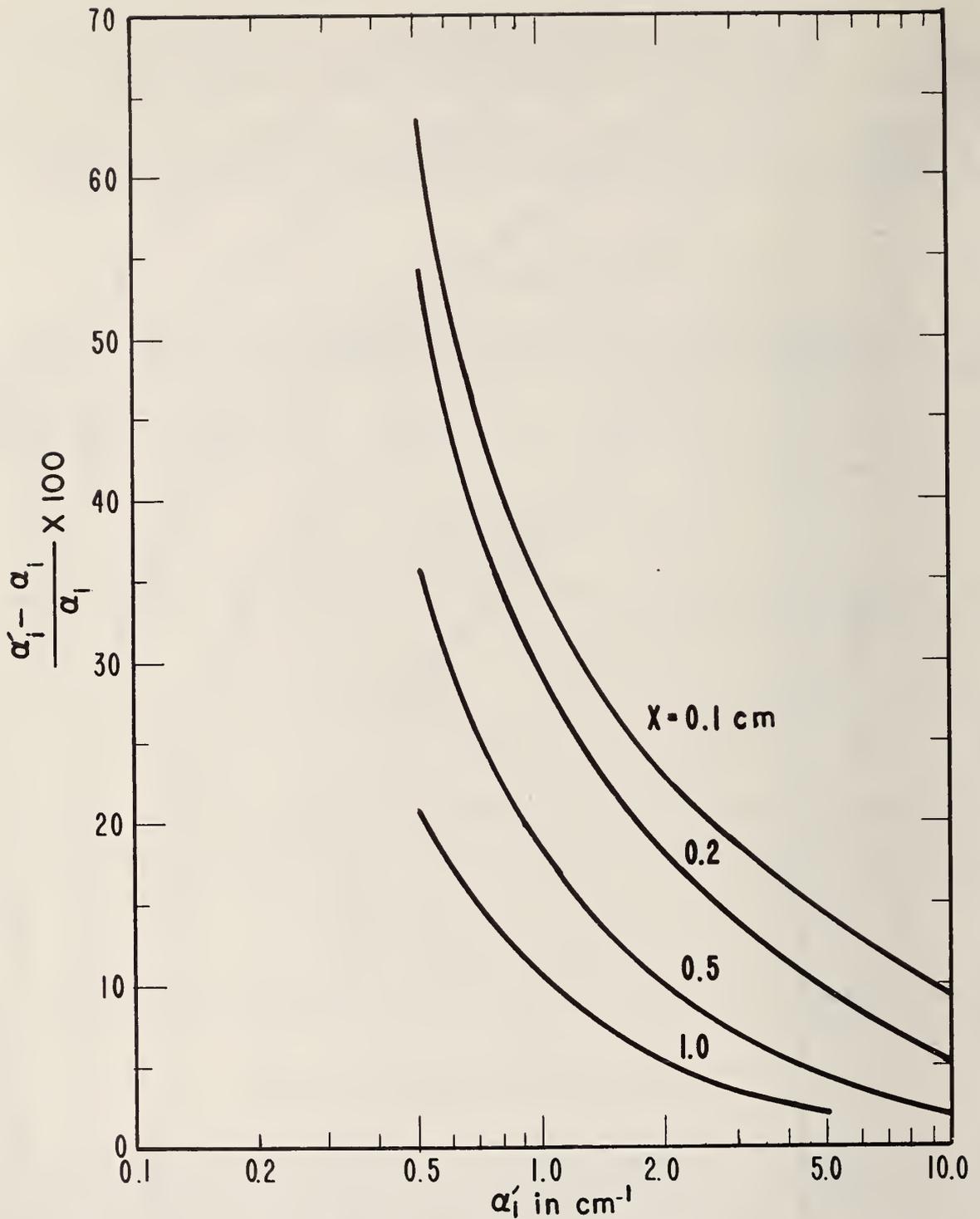limit of large $\alpha_i x$ no correction is needed of course.

Figure 5. Graph for the air reference method of the percent difference between the impurity absorption coefficient determined using the complete transmittance equation and that found from the approximate equation for several values of specimen thickness x. The constants used were $R = 0.2995$ and $\alpha_b = 0.8$ cm^{-1}, which are appropriate for the 9-μm oxygen band in silicon at 300 K.
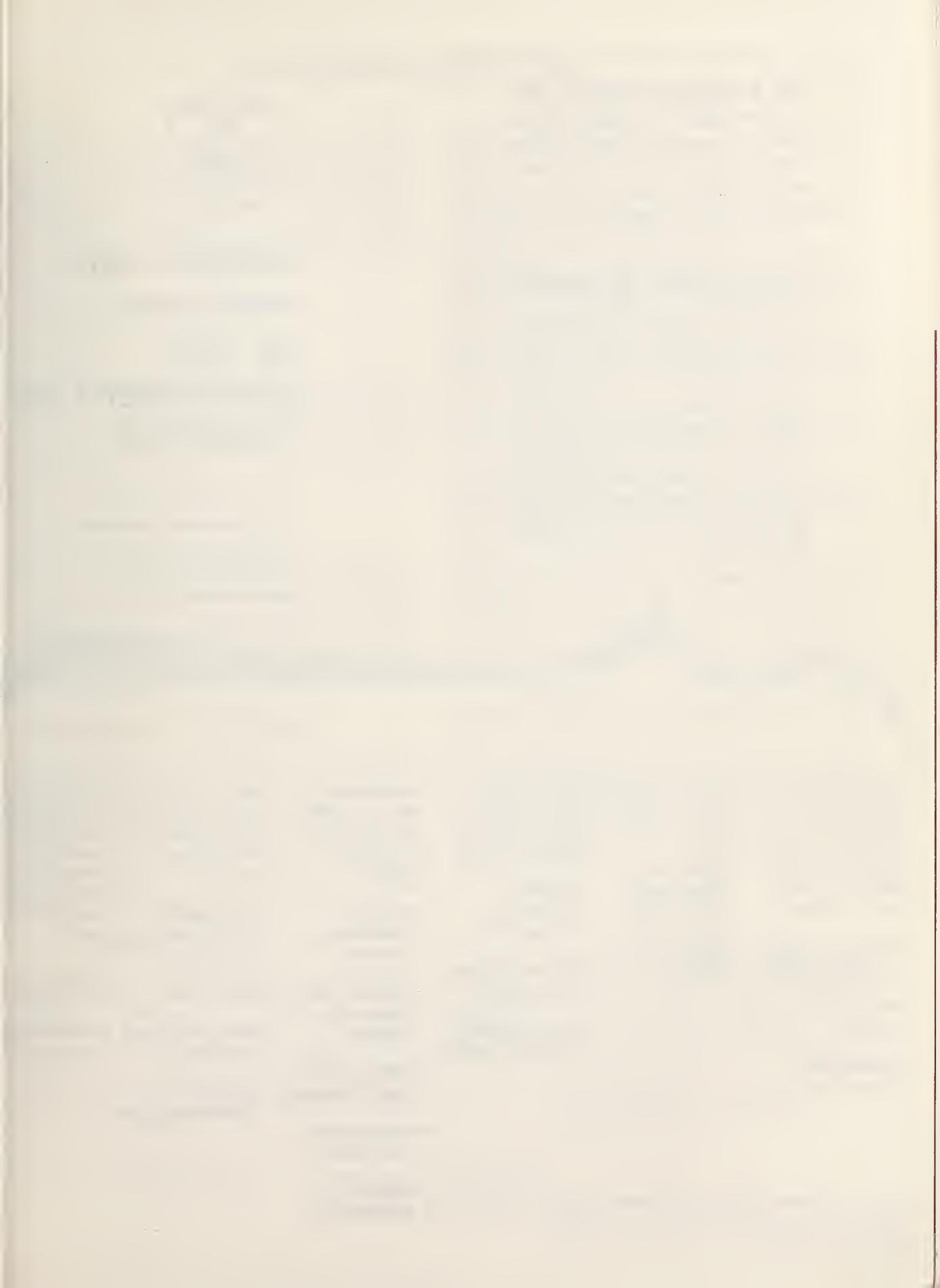
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NOTE: This schematic is neither an organization chart nor a program outline for budget purposes. It is a general statement of the Department's mission in relation to the national goal of economic development.

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