

# Refractive Index of ZnS, ZnSe, and ZnTe and Its Wavelength and Temperature Derivatives

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Refractive index data of ZnS, ZnSe, and ZnTe were searched, compiled, and analyzed. Recommended values of refractive index for the transparent spectral region were generated in the ranges 0.5–14  $\mu\text{m}$  and 93–1000 K for ZnS, 0.55–18  $\mu\text{m}$  and 93–618 K for ZnSe, and 0.55–30  $\mu\text{m}$  at room temperature for ZnTe. Generation of these values was based on a dispersion equation that best fits selected data sets covering wide temperature and wavelength ranges where the available experimental data permit. Temperature and wavelength derivatives of refractive index were calculated from the first derivatives of the equation with respect to temperature and wavelength, respectively. The results are in concordance with the existing data.

Key words: optical constants; refractive index; temperature coefficient of refractive index; zinc selenide; zinc sulfide; zinc telluride.

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### List of Symbols

$a$	Adjustable constant
$A$	Adjustable constant
$b$	Adjustable constant
$B$	Adjustable constant
$C$	Adjustable constant
$E$	Adjustable constant
$E_g$	Energy gap
$F$	A function of wavelength
$k$	Adjustable constant
$n$	Refractive index
$n_a$	Refractive index of ambient air
$N$	Oscillator strength
$R$	A function of wavelength
$S$	A function of wavelength
$t$	Temperature relative to 293 K
$T$	Absolute temperature

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### Greek Symbols

$\alpha$	Linear thermal expansion coefficient
$\delta$	Damping factor
$\epsilon$	Complex dielectric constant, value of dielectric constant
$\epsilon_1$	Real part of $\epsilon$
$\epsilon_2$	Imaginary part of $\epsilon$
$\epsilon_0$	Static dielectric constant
$\epsilon_\infty$	High-frequency dielectric constant
$\kappa$	Extinction coefficient; oscillator strength
$\lambda$	Wavelength of light
$\lambda_i$	Wavelength of the $i$ th absorption band
$\Delta$	Change in a quantity
$\omega$	Frequency
$\Omega$	Equals $\lambda_i/\lambda$

## 1. Introduction

The refractive index of a material is one of its fundamental and useful optical properties. Accurate knowledge of

refractive index over a wide range of wavelength and temperature is indispensable for many applications. Although this property continues to receive attention for its industrial as well as scientific applications, the current state of the

available data for many widely used materials is less than adequate. While experimental results for the refractive index of these materials are reported by many investigators claiming high internal accuracy and agreement, the data as a whole in many cases are in disagreement.

In this study, an attempt is made to consolidate all of the published refractive index data for zinc chalcogenides and to evaluate the raw experimental data and techniques of measurements. A modified Sellmeier-type dispersion relation is utilized to describe the available body of data. The resultant equations are used to generate the most probable values, which agree with the selected experimental data to within estimated uncertainties based on reported experimental errors.

## 2. Theoretical Background on Refractive Dispersion in Solids

### 2.1. Refractive Index

For pure substances, the wavelength or frequency dependence of the optical constants may be described by the classical treatment of Lorentz. The theory assumes the solid to be composed of a series of independent oscillators, which are set into forced vibrations by the incident radiation. The Lorentz theory of absorption and dispersion for both insulating and semiconducting materials is expressed by two familiar relations:

$$n^2 - \kappa^2 = 1 + \sum_i \frac{N_i \lambda_i^2 (1 - \Omega^2)}{(1 - \Omega^2)^2 + \delta_i^2 \Omega^2} \quad (1)$$

and

$$2n\kappa = \sum_i \frac{N_i \lambda_i^2 \delta_i \Omega}{(1 - \Omega^2)^2 + \delta_i^2 \Omega^2}, \quad (2)$$

where  $n$  is the refractive index,  $\kappa$  is the absorption index,  $N_i$  is the parameter associated with the strength of the  $i$ th oscillator,  $\lambda_i$  is the resonant wavelength of the  $i$ th oscillator,  $\delta_i$  is the damping factor of the  $i$ th oscillator,  $\Omega = \lambda_i/\lambda$ , and  $\lambda$  is the wavelength of incident radiation. In the transparent wavelength region, Eq. (1) can be reduced to the well-known Sellmeier-type equation by neglecting the absorption and the linewidth of the oscillators, thus leading to

$$n^2 = 1 + \sum_i \frac{a_i \lambda^2}{\lambda^2 - \lambda_i^2} + \sum_j \frac{b_j \lambda^2}{\lambda^2 - \lambda_j^2}. \quad (3)$$

Terms in the first summation are contributions from the ultraviolet absorption bands and those in the second are from the infrared absorption bands. From Eq. (3), the optical and static dielectric constants,  $\epsilon_\infty$  and  $\epsilon_0$ , of the material under consideration are defined as

$$\epsilon_\infty = 1 + \sum_i a_i \quad (4)$$

and

$$\epsilon_0 = 1 + \sum_i a_i + \sum_j b_j.$$

In an ideal application of Eq. (3), one would need to know the wavelengths of all of the absorption bands in the absorption regions. This is very difficult in practice because

out of the large number of absorption bands, only a few of them are accessible for experimental observation. It is also observed that among the absorption bands, only those located closest to the transparent region have noticeable effect on the dispersion of the refractive index in the transparent region. In order to simplify the calculations of the effect due to unobserved absorption bands and those bands that have only a minor influence, the following approach is taken. Each term in the first summation from Eq. (3) is rewritten as

$$\frac{a_i \lambda^2}{\lambda^2 - \lambda_i^2} = a_i + \frac{a_i \lambda_i^2}{\lambda^2 - \lambda_i^2}. \quad (5)$$

Since  $\lambda_i$ 's are usually considerably smaller than  $\lambda$ 's in the transparent region, a good approximation of the first summation is

$$\sum_i \frac{a_i \lambda^2}{\lambda^2 - \lambda_i^2} = \sum_i a_i + \sum_i \frac{a_i \lambda_i^2}{\lambda^2 - \lambda_i^2} = \sum_i a_i + \frac{a_u \lambda_u^2}{\lambda^2 - \lambda_u^2}, \quad (6)$$

where  $a_u$  and  $\lambda_u$  are the effective quantities equivalent to the total contribution from all ultraviolet bands.

The terms in the second summation from Eq. (3) account for the effects of the absorption bands beyond the long wavelength limit of the transparent region. It is generally observed that only a single term due to the transverse optical mode (TO mode) of fundamental phonon at wavelength  $\lambda_1$  is sufficient to account for the effects. Therefore, the contribution from the second summation is simplified to

$$b_1 + \frac{b_1 \lambda_1^2}{\lambda^2 - \lambda_1^2}, \quad (7)$$

with  $b_1$  and  $\lambda_1$  associated with the TO mode phonon. Since refractive index data for zinc chalcogenides are also available in the region beyond the reststrahlen region between 100 and 600  $\mu\text{m}$ , this TO mode phonon should serve as the absorption band on the short wavelength side of this wavelength region. It is, therefore, conceivable that the refractive index data both above and below the reststrahlen band can be described by a single dispersion equation with some modification. In order to achieve such a result, the first consideration was to include a damping factor that would eliminate the singularity in Eq. (7). Equation (7) would then be replaced by the corresponding term in Eq. (1):

$$\frac{b_1 (1 - \Omega^2)}{(1 - \Omega^2)^2 + \delta^2 \Omega^2}, \quad (8)$$

where  $\Omega = \lambda_1/\lambda$ . However, the real data fitting calculations for zinc chalcogenides indicated negligibly small values for  $\delta$ .

Substituting Eqs. (6) and (7) into Eq. (3), we have the simplified dispersion equation at room temperature:

$$n^2 = \epsilon_0 + \frac{A}{\lambda^2 - \lambda_u^2} + \frac{B}{\lambda^2/\lambda_1^2 - 1}, \quad (9)$$

where  $A$  and  $B$  are treated as adjustable constants and  $B$  is related to the dielectric constants by the condition:

$$\epsilon_\infty = \epsilon_0 - B. \quad (10)$$

The parameters  $\epsilon_0$ ,  $A$ ,  $B$ ,  $\lambda_u$ , and  $\lambda_1$  in Eq. (9) can be expressed as functions of temperature based on the consider-

ations given below. There are four types of physical effects which influence the parameters in Eq. (9). First is the thermal expansion; the material becomes less dense as temperature increases. Were this the only mechanism operative, it would reduce the refractive index as temperature increased. The fact that the refractive index of zinc chalcogenides increases with temperature, implies that other mechanisms are predominant. Second are the thermal occupancies of the energy levels of the material as a function of temperature; the total number of oscillators varies with temperature. It is apparent that the thermal occupancies increase with temperature as evidenced by the observed positive values of  $\Delta n/\Delta T$ . Third is the change of refractive index of ambient air. Since the refractive index of a material is usually measured relative to air, i.e.,  $n/n_a$  is measured, to determine the temperature variation of refractive index of the material it is necessary to take into account the corresponding change in the refractive index of the ambient air. Thus,

$$\frac{d}{dT} \left( \frac{n}{n_a} \right) \simeq \frac{dn}{dT} - n \frac{dn_a}{dT}, \quad (11)$$

where  $dn_a/dT$  is about  $0.11 \times 10^{-5}$ . The second term in Eq. (11) is usually masked by the uncertainties in the data. Fourth are the thermal shifts of characteristic absorption bands. For most materials, both  $\lambda_u$  and  $\lambda_l$  increase with temperature. Both of these shifts tend to increase refractive index in the transparent region. In the extreme limits where  $\lambda$  is close to either  $\lambda_u$  or  $\lambda_l$ , the refractive index at  $\lambda$  increases rapidly with temperature. It is experimentally observed that  $\lambda_u$  is approximately a linear function of temperature<sup>1</sup> over a wide temperature region, as is  $\lambda_l$ .<sup>6</sup>

Since adequate expressions of thermal expansion and thermal occupancy of zinc chalcogenides as a function of temperature do not appear to be available and the correction due to index change of ambient air is approximately a constant, it is therefore possible to treat each of the parameters in Eq. (9) as a polynomial function of temperature to account for the first three effects combined. Thus, the parameters in Eq. (9) are replaced by

$$\begin{aligned} \epsilon_0(t) &= E(t) = E_0 + E_1 t + E_2 t^2 + E_3 t^3 + E_4 t^4, \\ A(t) &= A_0 + A_1 t + A_2 t^2 + A_3 t^3 + A_4 t^4, \\ B(t) &= B_0 + B_1 t + B_2 t^2 + B_3 t^3 + B_4 t^4, \\ \lambda_u(t) &= \lambda_{u0} + \beta_u t, \\ \lambda_l(t) &= \lambda_{l0} + \beta_l t, \end{aligned} \quad (12)$$

where  $t = T - 293$  K, and  $E$ 's,  $A$ 's,  $B$ 's, and  $\beta$ 's are constants with  $E_0, A_0, B_0, \lambda_{u0}$ , and  $\lambda_{l0}$  determined at 293 K, i.e., at  $t = 0$ . Only up to the fourth degree of  $t$  is retained in the above expressions as it was found that the inclusion of higher degrees or reducing to lower degrees did not yield adequate data fitting. With all these considerations, Eq. (9) can be expressed in a general form as

$$n^2(\lambda, t) = E(t) + \frac{A(t)}{\lambda^2 - \lambda_u^2} + \frac{B(t)}{\lambda^2/\lambda_l^2 - 1}, \quad (13)$$

which is reduced to Eq. (9) for  $T = 293$  K or  $t = 0$ .

Equation (13) is a preferred empirical expression for the refractive index in terms of both temperature and wave-

length as it identifies the physical meaning of various constants and it can be used to calculate derived quantities. Among other things, the dielectric constants at room temperature can be obtained from the values of  $E_0$  and  $B_0$ . If a sufficient amount of accurate data are available, the constants  $E$ 's and  $B$ 's can be determined and subsequently can be used to calculate the dielectric constants at other temperatures. With the constants appropriately determined,  $dn/dT$  or  $dn/d\lambda$  can easily be calculated by taking the first derivative of Eq. (13) with respect to  $T$  or  $\lambda$ . The use of  $t$  rather than the absolute temperature  $T$  is based on the fact that data on the refractive index and other related physical properties are readily available for room temperature. It is, therefore, appropriate to choose room temperature as the point about which temperature variation of the refractive index can be calculated, provided there is adequate temperature-dependent data.

## 2.2. Temperature Derivative of Refractive Index

Ramachandran<sup>2</sup> has presented a semiempirical theory of thermo-optical effects in crystals, in which the dispersion was fitted to experimental data. His theory employed a series of oscillator wavelengths and oscillator strengths as adjustable parameters. A relationship was found between temperature shifts of various parameters and fundamental oscillator wavelengths as shown below:

$$2n \frac{dn}{dT} = C - 3\alpha(n^2 - 1) + \sum_i F(\lambda, \lambda_i) \left( \frac{1}{\lambda_i} \frac{d\lambda_i}{dT} \right), \quad (14)$$

where  $C$  is effectively a constant over a limited temperature range and

$$F(\lambda, \lambda_i) = \frac{2k_i \lambda^4}{(\lambda^2 - \lambda_i^2)^2}$$

with  $k_i$  a constant. However, the parameters chosen were rather numerous and often not unique; no general prescription was presented for determining their temperature variations which are necessary for the calculation of  $dn/dT$ . Harris *et al.*<sup>3</sup> proposed an empirical relation without theoretical justification for the dispersion of  $dn/dT$ . It relates the observed values of  $dn/dT$  to the wavelength  $\lambda$  and the wavelength corresponding to energy gap  $\lambda_g$  by the expression:

$$\frac{dn}{dT} = aR^b, \quad (15)$$

where  $a$  and  $b$  are constants and  $R = \lambda^2/(\lambda^2 - \lambda_g^2)$ . This relation was later reexamined by Johnston<sup>4</sup> in light of some phenomenological calculations of Tsay *et al.*<sup>5</sup> in which the following equation was derived

$$2n \frac{dn}{dT} = K^2 \left( -3\alpha R + \frac{2}{\lambda_g} \frac{d\lambda_g}{dT} R^2 \right), \quad (16)$$

by neglecting the small contribution from the lattice. For practical data interpolation, Eq. (16) was simplified by Johnston to

$$2n \frac{dn}{dT} = AR + BR^2. \quad (17)$$

In comparison, one can notice that Eqs. (14) and (17) can be obtained by differentiating the second term of Eq. (9) with

respect to temperature. It should be pointed out that most published work<sup>2-5</sup> on semiconductors generally assumes that  $dn/dT$  data are nearly independent of temperature over a fairly wide range of temperature and that lattice contributions to  $dn/dT$  are negligible. No consideration has been given to the effect of thermal occupancies. As a result, much of the reported  $dn/dT$  data remains nearly a constant over a temperature range of a few hundred degrees. In real situations, however, all these assumptions become inadequate as discussed in a later section dealing with the available data.

Differentiating Eq. (13) with respect to temperature, we get

$$2n \frac{dn}{dT} = A_0 S_u + B_0 S_I + E_1 + E_2 p_2 + E_3 p_3 + E_4 p_4 + A_1 (R_u + S_u t) + A_2 (R_u p_2 + S_u t_2) + A_3 (R_u p_3 + S_u t_3) + A_4 (R_u p_4 + S_u t_4) + B_1 (R_I + S_I t) + B_2 (R_I p_2 + S_I t_2) + B_3 (R_I p_3 + S_I t_3) + B_4 (R_I p_4 + S_I t_4), \quad (18)$$

where  $p_2 = 2t$ ,  $p_3 = 3t^2$ ,  $p_4 = 4t^3$ ,  $t_2 = t^2$ ,  $t_3 = t^3$ ,  $t_4 = t^4$ ,

$$R_u = \frac{1}{\lambda^2 - \lambda_u^2},$$

$$S_u = \frac{dR_u}{dT} = \frac{2\lambda_u \beta_u}{(\lambda^2 - \lambda_u^2)^2},$$

$$R_I = \frac{1}{\lambda^2/\lambda_I^2 - 1},$$

$$S_I = \frac{dR_I}{dT} = \frac{2\lambda^2 \beta_I}{\lambda_I^3 (\lambda^2/\lambda_I^2 - 1)^2},$$

$$\lambda_u = \lambda_{u0} + \beta_u t, \text{ and } \lambda_I = \lambda_{I0} + \beta_I t.$$

Either Eq. (13) or Eq. (18) can be used for linear regression to determine the constants  $E$ 's,  $A$ 's, and  $B$ 's depending on the type and quality of available data; if reliable temperature-dependent  $dn/dT$  data are available, Eq. (18) should be used after the values of  $E_0$ ,  $A_0$ ,  $B_0$ ,  $\lambda_{u0}$ , and  $\lambda_{I0}$  have been determined at room temperature.

### 3. Presentation of Numerical Data

Reference values are generated here through critical evaluation, analysis, and synthesis of the available experimental data. The procedure involves critical evaluation of the validity and accuracy of the available data and information, resolution, and reconciliation of disagreements in cases of conflicting data, correlation of data in terms of various controlling parameters, curve fitting with theoretical or empirical equations, and comparisons of experimental values with predictions. No attempt has been made to analyze the data of thin films and in regions of strong absorption, because of the scantiness of reliable information. However, experimental data on thin films and in absorption regions are also presented, along with those of the transparent region, in figures for the purpose of comparison and completeness.

A number of figures summarize the information and give data as a function of wavelength and temperature. The conventions used in this presentation, and specific com-

ments concerning the interpretation and use of the data are given below. The subsections for each substance contain all available information and data for a given material and cover the following:

- (a) A text discussing the data, analysis, and recommendations;
- (b) A figure of experimental  $n$  values (wavelength and temperature dependence);
- (c) A figure of experimental  $dn/dT = f(\lambda)$ ;
- (d) A figure of experimental  $dn/dT = f(T)$ ;
- (e) Figures of recommended values of  $n$ ,  $dn/dT$ , and  $dn'/d\lambda$ ;
- (f) Tables of recommended values of  $n$ ,  $dn/dT$ , and  $dn/d\lambda$ .

Since a reader might be interested in a specific substance, it was considered desirable to include important information and discussion in each subsection even though some of the subject matter found in other subsections may be repeated. In figures containing experimental data, selected data sets are labeled by appropriate legends.

Dispersion equations for each of the substances have been proposed from time to time in earlier studies. These available relations are collectively presented in a table to facilitate comparison. Refractive indices for most of selected data sets are reported to the fourth decimal place. However, detailed compositions and characterizations of the specimens were usually not clearly given. Since impurities in the sample and conditions of the surface are factors affecting the accuracy of the observed results, such highly precise data cannot be applied to a sample chosen at random. For this reason, no attempt is made to recommend any particular set of data with the reported high accuracy, but to generate the most probable values for the pure samples. As a result, the estimated uncertainties in the recommended values on the refractive index are higher than those reported for the data obtained by high-precision measurements.

### 3.1. Zinc Sulfide, ZnS

There are 59 sets of experimental data available for the refractive index (wavelength dependence + temperature dependence) of zinc sulfide as plotted in Figs. 1 and 2. Some of the data sets for thin films or multilayers are included here for the purpose of comparison. With the exclusion of largely discrepant and scattered data due to either inadequate specimen or unreliable method, the data sets reported by Mell,<sup>8</sup> DeVore,<sup>9</sup> Czyzak *et al.*,<sup>10-12</sup> Bond,<sup>15</sup> Manabe *et al.*,<sup>16</sup> Feldman *et al.*,<sup>17</sup> and Wolfe and Korniski<sup>18</sup> are considered representative for the available refractive index of zinc sulfide in the fundamental transparent region. Data sets reported by Hattori *et al.*<sup>19</sup> are the only available material in the wavelength range from about 100 to 650  $\mu\text{m}$ . Data of hexagonal ZnS crystals were measured by Bieniewski and Czyzak<sup>14</sup> and by Piper *et al.*<sup>13</sup>

#### 3.1.1. Review of Available Data

Early measurements on the refractive index of ZnS over the visible spectrum covering a large temperature range were reported by Mell<sup>8</sup> for samples of natural crystal, a sphalerite

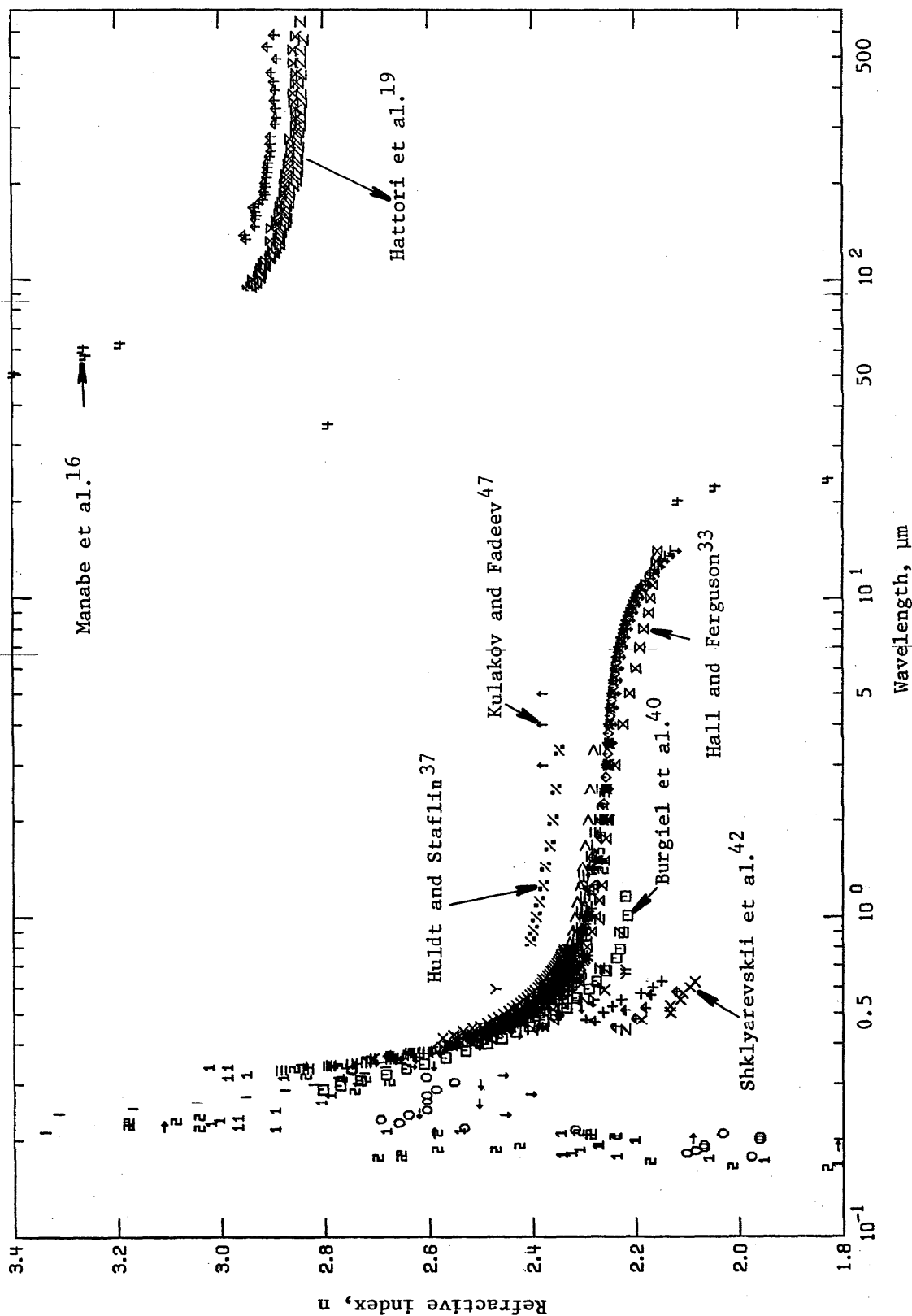


Figure 1. Available experimental refractive index of ZnS (wavelength dependence).

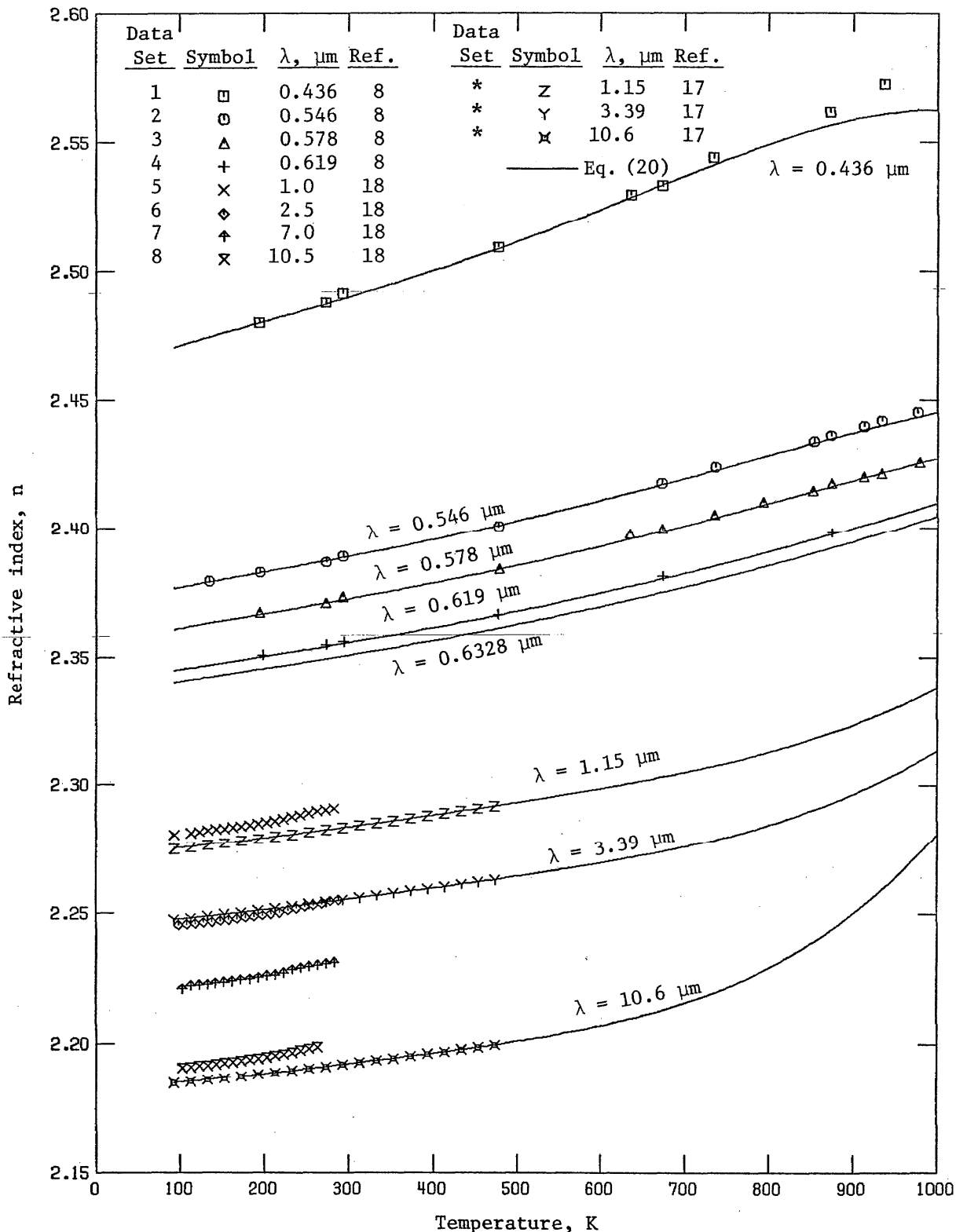


Figure 2. Experimental and calculated refractive index of ZnS (temperature dependence). Data set "\*" are derived from  $dn/dT$  data.

Table 1. Comparison of dispersion equations proposed for ZnS

Source	Wavelength and temperature ranges	Dispersion equation $\lambda$ in $\mu\text{m}$ , $\Omega = \lambda_T/\lambda$
Mell, M., 1923; Ref. 8	0.4162-0.7320 $\mu\text{m}$ 273 K	$n^2 = 3.0221 + \frac{2.0998 \lambda^2}{\lambda^2 - (0.2532)^2}$
DeVore, J.R., 1951; Ref. 9	0.3650-1.5296 $\mu\text{m}$ 298 K	$n^2 = 5.164 + \frac{0.1208}{\lambda^2 - (0.27055)^2}$
Czyzak, S.J., Baker, W.M., Crane, R.C., and Howe, J.B., 1957; Ref. 10	0.44-1.4 $\mu\text{m}$ 298 K	$n^2 = 5.131 + \frac{0.1275}{\lambda^2 - (0.27055)^2}$
Czyzak, S.J., Payne, H., Crane, R.C., and Baker, W.M., 1957; Ref. 11	0.365-4.0 $\mu\text{m}$ 300 K	$n^2 = 5.0475 + \frac{0.2645}{\lambda^2} - \frac{0.0947}{\lambda^4} + \frac{0.0427}{\lambda^6}$ $- \frac{0.0079}{\lambda^8} + \frac{0.0005}{\lambda^{10}}$
Manabe, A., Mitsubishi, A., Yoshinaga, H., 1967; Ref. 16	19-62 $\mu\text{m}$ 300 K	$n^2 - k^2 = \epsilon_\infty + \frac{N(1-\Omega^2)}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ $2nk = \frac{N\delta\Omega}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ for cubic structure: $\epsilon_\infty = 5.7$ , $\lambda_I = 35.46$ , $\delta = 0.024$ , and $N = 3.2$ for hexagonal structure: $\epsilon_\infty = 5.7$ , $\lambda_I = 36.496$ , $\delta = 0.017$ , and $N = 3.9$
Kodak publication U-72, 1971; Ref. 21	1.0-13.0 $\mu\text{m}$ 300 K	$n = 2.2569735 + \frac{3.2640935 \times 10^{-2}}{\lambda^2 - 0.028}$ $+ \frac{6.0314637 \times 10^{-4}}{(\lambda^2 - 0.028)^2}$ $- 5.2705532 \times 10^{-7}\lambda^4$ $- 6.0428638 \times 10^{-7}\lambda^4$
Hattori, T., Homma, Y., Mitsubishi, A., and Tacke, M., 1973; Ref. 19	134-584 $\mu\text{m}$ at 300 K 132-578 $\mu\text{m}$ at 80 K 92-641 $\mu\text{m}$ at 2 K	$n^2 = \frac{\epsilon_0 - \epsilon_\infty \Omega^2}{1 - \Omega^2}$ at 300 K: $\epsilon_0 = 8.34$ , $\epsilon_\infty = 4.7$ , and $\lambda_I = 38.462 \mu\text{m}$ ; at 80 K: $\epsilon_0 = 8.10$ , $\epsilon_\infty = 4.8$ , and $\lambda_I = 38.168 \mu\text{m}$ ; at 2 K: $\epsilon_0 = 8.04$ , $\epsilon_\infty = 4.9$ , and $\lambda_I = 38.023 \mu\text{m}$ .
Feldman, A., Horowitz, D., Waxler, R.M., and Dodge, M.J., 1978; Ref. 17	0.55-10.60 $\mu\text{m}$ 295 K	$n^2 = 1 + \sum_{i=1}^3 \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}$ for one sample at 294.6 K: $A_1 = 0.33904026$ $A_2 = 3.7606868$ $A_3 = 2.7312353$
Feldman, A., et al., 1978; Ref. 17, cont.		$\lambda_1 = 0.31423026$ $\lambda_2 = 0.17594174$ $\lambda_3 = 33.886560$ for second sample at 294.9 K: $A_1 = 0.24199447$ $A_2 = 3.8575584$ $A_3 = 2.5433609$ $\lambda_1 = 0.33005445$ $\lambda_2 = 0.17899635$ $\lambda_3 = 32.849275$
Present work, 1982	0.5-14.0 $\mu\text{m}$ 93-618 K	$n^2(\lambda, t) = E(t) + \frac{A(t)}{\lambda^2 - \lambda_u^2} + \frac{B(t)}{\lambda^2/\lambda_I^2 - 1}$ $t = T - 293$ See Eq. (20) in text for the expressions of $\lambda_u$ , $\lambda_I$ , $E(t)$ , $A(t)$ and $B(t)$ .



with green hue. These data indicate that not only is the dispersion of ZnS very large, but also the refractive index varies appreciably with temperature. At room temperature,  $n$  changes from 2.5240 at wavelength  $0.4162 \mu\text{m}$  to  $2.3263$  to  $0.732 \mu\text{m}$ ; while at wavelength  $0.546 \mu\text{m}$ ,  $n$  varies from  $2.3867$  at  $273 \text{ K}$  to  $2.4452$  at  $977 \text{ K}$ . Several prismatic specimens were used, and the results were consistent to the third decimal place. Mell also showed that the data at  $273 \text{ K}$  can be fitted by a Sellmeier-type formula as given in Table 1, and the data at several selected wavelengths were found to vary quadratically with temperature.

DeVore<sup>9</sup> measured refractive indices for a clear, water-white natural sphalerite crystal at room temperature over a wavelength region between  $0.365$  and  $0.578 \mu\text{m}$  and at  $1.5296 \mu\text{m}$ . The data points fitted well to a dispersion equation (see Table 1) similar to that of Mell. Numerically the data from these two sources are discrepant in the overlapped region by several units in the third decimal place which may be attributed to the impurities and experimental errors. Both dispersion equations of Mell and of DeVore suggest an effective ultraviolet absorption band at about  $0.27 \mu\text{m}$  and do not account for the contribution from infrared absorption bands. It should be pointed out that in spite of the fact that DeVore's data are represented by a simple equation, the predicted refractive indices at wavelengths near  $1.5296 \mu\text{m}$  are not reliable. At that wavelength, the effect from infrared absorption bands is significant and negative; a simple dispersion equation without taking into account the effect from infrared will predict a higher result as can be seen by comparison with the data of Czyzak *et al.* and Feldman *et al.*

Bond<sup>15</sup> attempted precise measurements significant to the fourth decimal place on the refractive index of ZnS over the wavelength range  $0.45$ – $2.4 \mu\text{m}$  using the minimum deviation method. A natural specimen from San Antander, Spain was not transparent beyond  $2.4 \mu\text{m}$ . His data were quite consistent in comparison with the data reported by Feldman *et al.*, and the discrepancy in the overlapped wavelength region was within two units in the third decimal place.

Refractive index data of synthetic single cubic crystals of ZnS covering a spectral range from  $0.365$  to  $4.0 \mu\text{m}$  at room temperature are given in four references.<sup>10–12,20</sup> These data sets were measured basically by the same group of investigators but over a number of years. Spectroscopic analysis of the crystals showed a total analyzed impurity content of less than  $0.0001\%$ , indicating that the data obtained were supposedly for pure single cubic crystal but for unknown reasons the data showed large discrepancies. The data in the visible region were fitted to a Sellmeier-type dispersion equation, and for the extended wavelength region, the data were fitted to a polynomial equation of negative even powers of wavelength as shown in Table 1. When compared with the data reported by Mell and by DeVore, the differences are in the third to second decimal place and show a large scattering. It is interesting to note that the dispersion equation for the visible region is very similar to that found by DeVore and both indicate an effective ultraviolet absorption band at  $0.2755 \mu\text{m}$ .

Manabe *et al.*<sup>16</sup> studied optical constants in the reststrahlen region,  $20 \mu\text{m}$  up to about  $100 \mu\text{m}$ , by means of

infrared lattice reflection spectra. Both synthetic cubic and hexagonal crystals were investigated and the spectra were analyzed using the Drude dispersion relation. The oscillator strength  $N$ , optical dielectric constant  $\epsilon_\infty$ , damping factor  $\delta$ , and wavelength of transverse optical phonon  $\lambda_1$ , in the Drude equations shown in Table 1 were determined by a least-squares fit of reflectivity data. In the case of hexagonal crystal, the wavelength of TO mode phonon is the same for both polarizations. The TO mode phonon wavelength was also obtained directly from transmission spectrum of an evaporated thin film and was found to be in good agreement with that obtained from the reflection spectra analysis. The static dielectric constant  $\epsilon_0$  was determined by substituting  $\lambda = \infty$  in the resulting Drude equation assuming zero absorption, i.e.,  $\epsilon_0 = n^2 = \epsilon_\infty + N\lambda_1^2$ .

Refractive index of CVD ZnS was measured by Feldman *et al.*<sup>17</sup> as part of the effort in the characterization of high-power laser window materials. Two CVD ZnS samples were measured by the high-precision minimum deviation method over a wide wavelength region ( $0.55$ – $10.6 \mu\text{m}$ ) of laser interest. The room-temperature data were reported to the fifth decimal place and were fitted to a three-term Sellmeier-type dispersion equation (shown in Table 1). Since the parameters in their dispersion equation were not intended to have physical significance but to be a mathematical fit to the observed data, the parameter values determined for these two samples were considerably different though the difference in refractive indices at any one wavelength was only about one unit or less in the fourth decimal place. In view of the reported average absolute residuals of  $n$  from the best-fit equation of each data set,  $5.4 \times 10^{-5}$  and  $4.6 \times 10^{-5}$ , respectively, the difference of one unit in the fourth decimal place should be regarded as experimental uncertainty and either of the two data sets closely represents the refractive index of CVD ZnS at room temperature.

Wolfe and Korniski<sup>18</sup> reported data for a sample of Irtran 2, a hot-pressed microcrystalline compact of ZnS, over a spectral region between  $0.6328$  and  $14 \mu\text{m}$  at room temperature and at  $84.9 \text{ K}$ . The precision of the measurement is a few parts in the fourth decimal place, namely  $2.86 \times 10^{-4}$  rms deviation. Intercomparison with the data of Irtran 2 reported earlier by Eastman Kodak Co.<sup>21</sup> reveals discrepancies of as much as  $4.8 \times 10^{-3}$  at the shorter wavelengths decreasing to  $2.8 \times 10^{-3}$  at the longer wavelengths; this is an order of magnitude larger than the experimental uncertainty. Such a difference is attributed to the sample itself. Comparison of the data sets of Irtran 2 and CVD ZnS is shown in Fig. 3 where the data of Irtran 2 disagree with those of CVD ZnS by amounts far more than the claimed experimental uncertainties.

Data of ZnS in the far infrared spectral range from  $100$  to  $600 \mu\text{m}$  were measured by Hattori *et al.*<sup>19</sup> at temperatures  $2$ ,  $80$ , and  $300 \text{ K}$ . The crystal used in the experiment was a mixed cubic and hexagonal. The data were described by a simple dispersion equation, shown in Table 1, for an undamped harmonic oscillator from which the dielectric constants and wavelength of TO mode phonon were determined with least-squares fit. The static dielectric constant serves as a check for the values obtained from various optical meth-

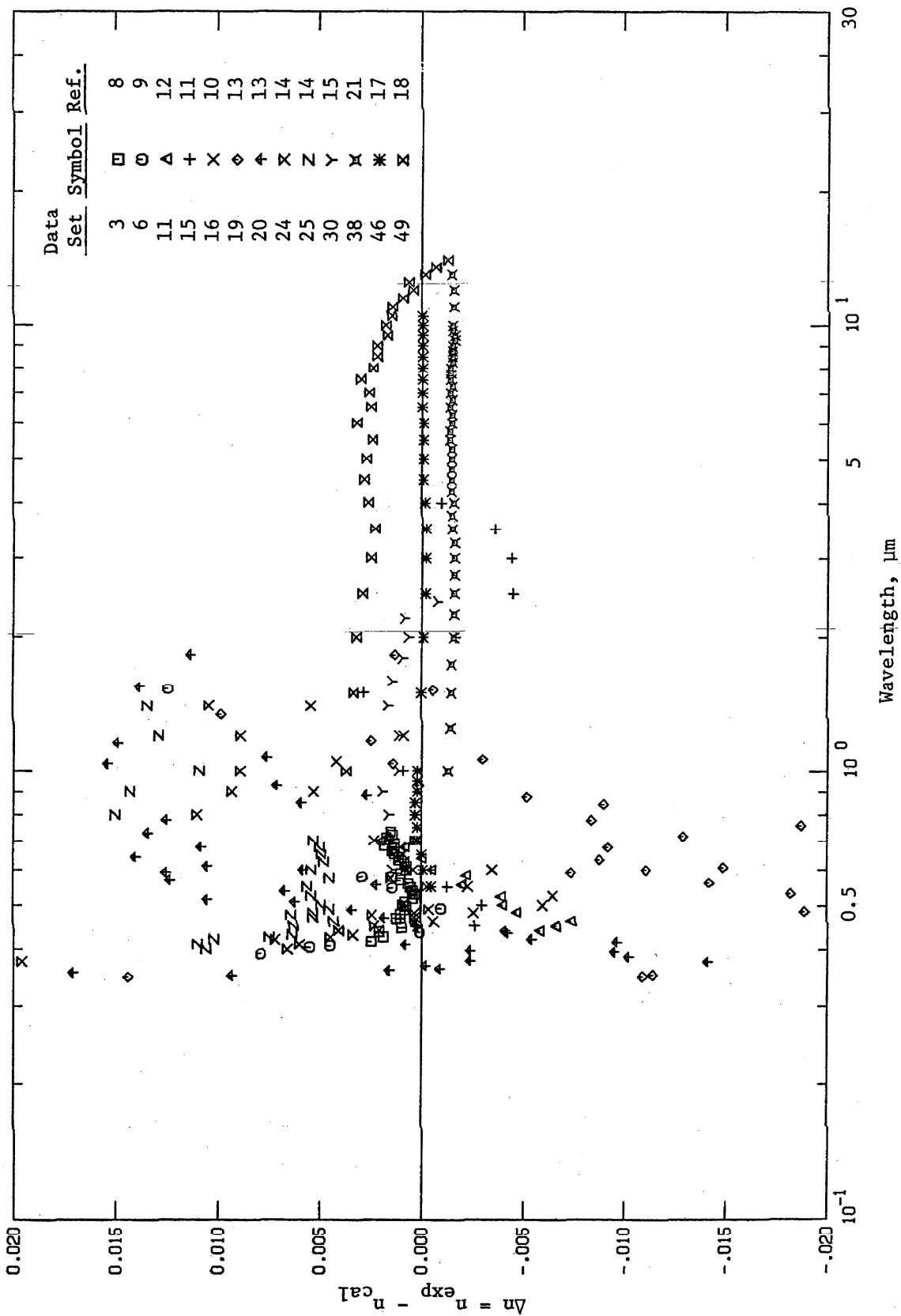


Figure 3. Comparison of experimental and calculated refractive index values of ZnS at room temperature. The calculated values from Eq. (19) are represented by the line  $\Delta n = 0$ .

ods. Since the data were measured by an interference method, the value of  $\epsilon_0$  obtained in the long wavelength region is believed to be reliable and should be adopted as a known parameter in the dispersion equation of ZnS.

Data for hexagonal ZnS crystals were reported by Bieniewski and Czyzak<sup>14</sup> over a wavelength range from 0.36 to 1.4  $\mu\text{m}$  and by Piper *et al.*<sup>13</sup> over a wavelength range from 0.33 to 1.8  $\mu\text{m}$ . In both investigations, the birefringence of hexagonal crystals was found to be small, about 0.006, and was fairly constant throughout the wavelength region investigated. They stated that within experimental error the dispersion equations proposed by DeVore<sup>9</sup> and by Czyzak *et al.*<sup>10</sup> were valid for both cubic and hexagonal crystals.

For ease of comparison, the deviations of the above mentioned data sets from the recommended values in the fundamental transparent region at room temperature are plotted in Fig. 3. It is obvious that the disagreement among the data sets reported by different investigators is greater than the accuracy claimed by each of them. Internal consistency was observed in each investigation; therefore, unaccounted sources of errors still exist that are responsible for these discrepancies.

### 3.1.2. Room-Temperature Dispersion Equation

In the present work, Eq. (9) is used to represent the room-temperature refractive index of ZnS. The appropriate parameters,  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_1$ , must be selected and the coefficients  $A$ ,  $B$ , and the parameter  $\lambda_u$  determined. Most important of all is the selection of reliable data sets used for input to fit Eq. (9). The selected data sets are limited to the works of Feldman *et al.*,<sup>17</sup> Mell,<sup>8</sup> and Hattori *et al.*<sup>19</sup> The data of Feldman *et al.* cover a wide spectral region and are measured with high accuracy. The data of Mell cover extended short wavelengths and a wide temperature region. Although the former measured CVD samples and the latter measured natural crystals, the two can be spliced together based on the following two facts. First, because the birefringence of CdS is small as discussed earlier, the refractive index data of single crystal and polycrystalline samples should agree closely. Second, the room-temperature data from these two sources in the overlapped region are consistent to the third decimal place which is within the experimental error of Mell's data. The data set reported by Hattori<sup>19</sup> is used to substantiate the correctness of the static dielectric constant for the infrared term.

The literature values of  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_1$  are very discrepant as shown in Table 2 where room-temperature  $\epsilon_\infty$  values vary from 4.7 to 5.7. For refractive index calculations accurate to the third or fourth decimal place, this variation is far too great. However, better values of  $\epsilon_\infty$  can be obtained from dispersion equations covering the visible region as proposed by various investigators. From Table 1, these  $\epsilon_\infty$  values are 5.1219 by Mell, 5.164 by DeVore, 5.131 and 5.0475 by Czyzak *et al.*, and 5.0096 by Feldman *et al.* A value close to 5.1 appears to be consistent.

The values of  $\epsilon_0$  vary from 8.34 to 8.9 for cubic ZnS (Table 2) which is too wide a range for refractive index calculations. The two available dispersion equations fail for  $\epsilon_0$  due to the lack of data beyond 10.6  $\mu\text{m}$  needed to provide ade-

Table 2. Available data on  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_1$  of ZnS

Temp., K	$\epsilon_\infty$	$\epsilon_0$	$\lambda_1$ , $\mu\text{m}$	Ref.	Remarks
300	5.7	8.9	35.46, 36.76	16	cubic
300	5.7	9.6	36.50	16	hexagonal
300		8.37		24	
300	5.13			25	
300			36.90	26	
300	4.7	8.34	38.46	19	
300			32.26	27	cubic
300			33.33	27	hexagonal
300		8.7		28	
80	4.8	8.10	38.17	19	
80		8.14		24	
2	4.9	8.04	38.02	19	

quate dispersion in the infrared term. However, the refractive index data in the 100 to 600  $\mu\text{m}$  region as reported by Hattori *et al.*<sup>19</sup> can be used to determine  $\epsilon_0$ . Although the dispersion equation obtained from this data set predicts a low value of  $\epsilon_\infty$  due to the lack of dispersion, the  $\epsilon_0$  calculated from the square of refractive index at the long wavelength end should be close to the static dielectric constant. Since the refractive index values in this data set vary from 2.95 at 100  $\mu\text{m}$  to 2.89 in the wavelength range from 300 to 600  $\mu\text{m}$ , it is reasonable to assume a value of  $\epsilon_0$  of about 2.89<sup>2</sup> or 8.35.

Among the values of  $\lambda_1$  in Table 2, the values reported by Manabe *et al.* are chosen. One of these values was obtained from transmission measurements on evaporated thin films, a type of measurement that provides direct means for determining  $\lambda_1$ . Additional supporting evidence for this value was obtained by Mathieu and Mathieu<sup>22</sup> from Raman measurements. The correct value of  $\lambda_1$  is most likely within the range 35.46–36.76  $\mu\text{m}$ .

Cardona and Harbeke<sup>23</sup> investigated band structure of cubic and hexagonal ZnS crystals in the spectral region below 0.41  $\mu\text{m}$ . It was observed that there was a striking similarity in the spectra of the optical constants, indicating a small difference in the arrangement of the atoms in the two crystals. Although only small differences are observed in optical constants, there are some fine structure differences in the absorption spectra. In all cases, a weak absorption peak is located at about 0.33  $\mu\text{m}$  and a strong absorption peak at about 0.23  $\mu\text{m}$  with a number of strong peaks at shorter wavelengths. This finding is consistent with the dispersion equations found earlier by others based on an effective absorption band at about 0.27  $\Omega\text{m}$ . The values of  $\lambda_u$  in Eq. (9) should be approximately in the range from 0.23 to 0.27  $\mu\text{m}$  but closer to 0.23  $\mu\text{m}$  to account for the effect of the infrared term. This is supported by the findings of Hall<sup>34</sup> and Cox *et al.*<sup>36</sup> who, in investigations on vacuum deposited films, found the refractive index curve has a maximum at about 0.23  $\mu\text{m}$ .

With all the essential parameters discussed above at hand, the selected data are fitted to Eq. (9) for the determination of the constants  $A$  and  $B$  by letting the parameters vary within their corresponding estimated limits. The dispersion equation for ZnS at room temperature thus obtained is

$$n^2 = 8.34096 + \frac{0.14540}{\lambda^2 - (0.23979)^2} + \frac{3.23924}{\lambda^2/36.525^2 - 1}, \quad (19)$$

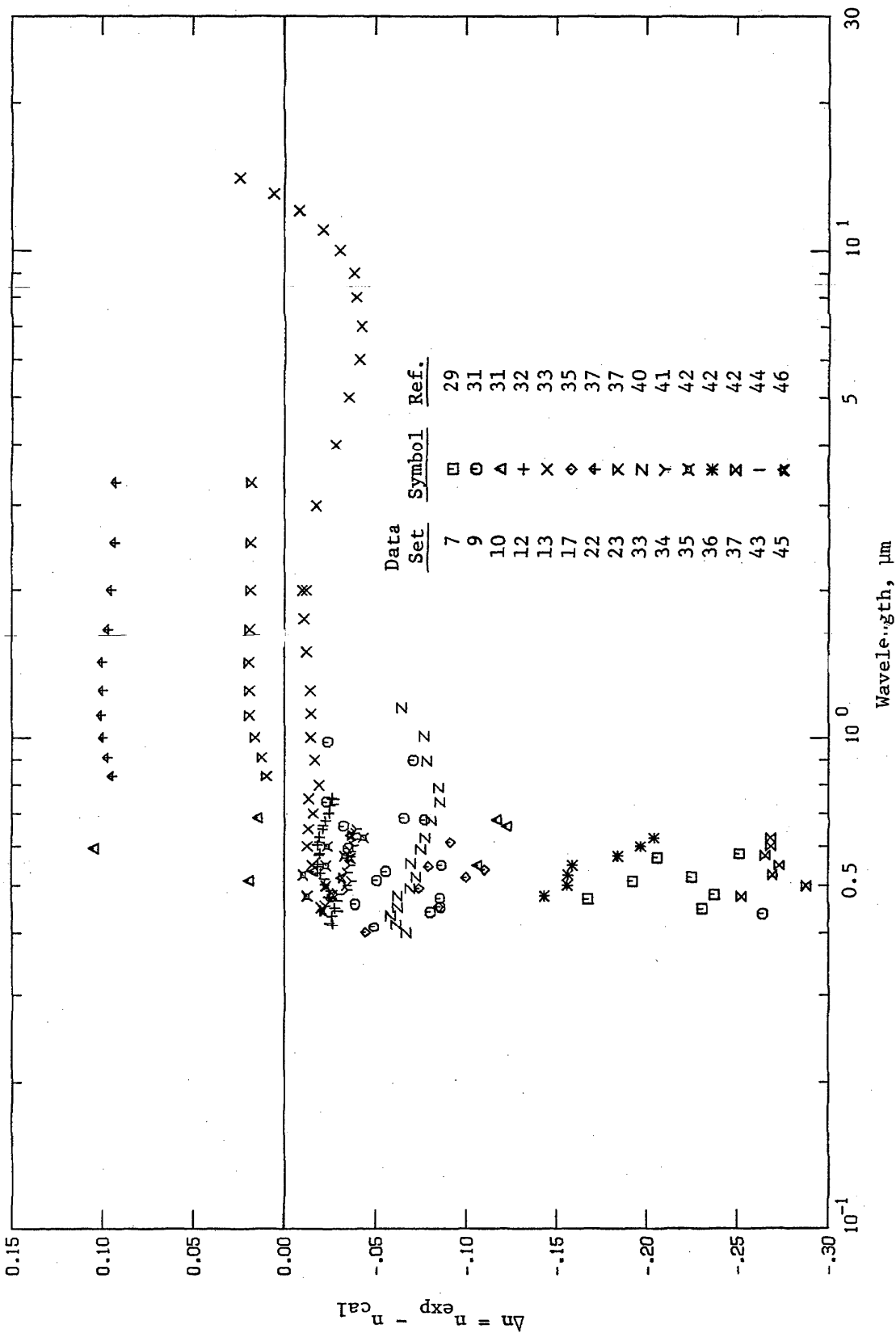


Figure 4. Comparison of experimental refractive indices of ZnS films and calculated values for bulk ZnS from Eq. (19). The calculated values are represented by the line  $\Delta n = 0$ .

where  $\lambda$  is in units of  $\mu\text{m}$ . This equation also serves as a starting point to formulate a generalized dispersion equation for temperature-dependent data as Eq. (13).

Equation (19) is valid in the wavelength range 0.5–14  $\mu\text{m}$  for CVD ZnS and in the wavelength range 0.5–2.4  $\mu\text{m}$  for natural ZnS. In Fig. 3, deviations of available room-temperature data from those calculated with Eq. (19) are plotted for visual comparison. It is clearly shown that data of synthetic crystals in the short wavelength region are largely scattered as expected while the data of Mell<sup>8</sup> and of Bond<sup>15</sup> show consistent deviation of less than 0.0016 and have the same dispersion as that of Eq. (19). In the long wavelength region, the data of Irtran 2 from Kodak publication U-72<sup>21</sup> indicate a constant deviation of about  $-0.0015$  throughout the wavelength range 1–13  $\mu\text{m}$  but the data for the same material reported later by Wolfe and Korniski<sup>18</sup> show a constant deviation of about  $+0.0025$  in the region below 10  $\mu\text{m}$  and a high dispersion in the region between 10 and 14  $\mu\text{m}$ . While the deviation of data of Mell and of Bond can be attributed to the experimental error and to the impurity content of the samples, the deviations of data for Irtran 2 samples is not due to experiment alone. As Wolfe and Korniski point out, it is probable that these deviations are caused by the differences in material from different batches. The constant deviation of the data sets mentioned above renders support to the validity of Eq. (19) as far as the dispersion of ZnS is concerned.

The causes of large deviations of synthetic crystal data and Irtran 2 data deserve further discussion. It is believed that these synthetic crystals investigated two decades ago contained considerable amount of impurities and defects unknown then. Although the techniques of crystal growth has since been improved, there are no new direct measurements reported. At present, there is no reliable data of crystalline ZnS to substantiate the validity of Eq. (19). Irtran 2 is a hot-forged substance; it is inevitable that impurities and voids are introduced during the forging processes. The result is the discrepant data from different batches.

No attempt was made to analyze the available data for thin films<sup>29-46</sup> since their refractive properties are affected by many factors that do not easily permit adequate characterization. Consequently, results of different investigators are often conflicting and inconsistent. The pressure and type of residue gas during deposition, the temperature of the substrate during deposition, the rate of deposition, the thickness of the film, the heat treatment after deposition, and aging are all important factors. In general, the refractive index data of a film deposition in high vacuum tend to be lower than that of the bulk because the observations are actually made on a combination of ZnS plus voids easily observed under an electron microscope. On the other hand, high refractive indices are obtained for thin films that are oxidized during deposition or are aged in the presence of undesirable residual gases or physical environments. However, it has been observed that the refractive index of a thin film tends to agree with the bulk index if the films are deposited under high vacuum on substrates maintained at elevated temperatures during deposition, followed by appropriate annealing. Figure 4 shows the deviations of experimental film data from the bulk data

calculated from Eq. (19). Although there is a disagreement in the refractive index values, most of the available film data generally follow a normal dispersion curve. It can be safely said that a properly prepared film sample should have the same dispersion characteristics as that of a bulk sample though having different refractive index values. In other words, the deviation should be nearly a constant as indicated in Fig. 4.

Equation (19) is also valid in the wavelength region 133–585  $\mu\text{m}$ . The averaged differences between the experimental data and the calculated values are of the order of  $\pm 0.006$ . The dispersion in this region is rather small as the difference of two extreme refractive indices is only 0.055 but the uncertainty in the data is rather large (of the order  $\pm 0.005$ ) as the data were digitized from a graph of low resolution. Under such condition, the reliability of the digitized values is compatible with the calculated ones.

### 3.1.3. Temperature-Dependent Dispersion Equation

Data on the temperature-dependent refractive index is very scanty. Data plotted in Fig. 2 are those of Mell<sup>8</sup> and Wolfe and Korniski.<sup>18</sup> Additional data sets plotted in Fig. 2 were derived from the  $dn/dT$  data reported by Feldman *et al.*<sup>17</sup> (see Figs. 5 and 6). Although the data sets by Mell cover a wide temperature range from 135 up to 979 K, they cover only the visible wavelengths. Mell's data in the short wavelength region below 0.5  $\mu\text{m}$  are not reliable because the material contains impurities evidenced by the greenish color of the sample. At high temperatures, the uncertainties are expected to be larger because the effects of impurities are expected to increase with temperature.

Refractive index data reported by Wolfe and Korniski cover a temperature range from 84.9 to 295.9 K and a wavelength range from 1 to 14  $\mu\text{m}$  from which they calculated  $dn/dT$  values. Since the claimed precision of their refractive index measurement is about  $\pm 3 \times 10^{-4}$  and the  $dn/dT$  value is in the order of  $\pm 5 \times 10^{-5} \text{K}^{-1}$ , each  $dn/dT$  value thus determined at temperature intervals of  $10^\circ$  has an error of about  $\pm 6 \times 10^{-5} \text{K}^{-1}$  associated with it. This large error masked the detail variation of  $dn/dT$  with temperature and wavelength; only average values could be obtained. For the wavelengths 1.0, 2.5, 7.0, and 10.5  $\mu\text{m}$ , the average  $dn/dT$  values vary linearly with temperature from  $3.5 \times 10^{-5} \text{K}^{-1}$  at 100 K to  $7.6 \times 10^{-5} \text{K}^{-1}$  at 280 K. Lacking, then, in detailed wavelength variation, these data are not used for data analysis but a rough comparison.

Although Feldman *et al.* reported only room-temperature refractive index, their  $dn/dT$  data are reliable to calculate the refractive index values at other temperatures from 93 to 473 K. The  $dn/dT$  data were measured by an interferometric technique at three discrete laser wavelengths: 1.15, 3.39, and 10.6  $\mu\text{m}$ . The shift of Fizeau interference fringes as a function of temperature, starting from room temperature, was observed and the corresponding  $dn/dT$  value was determined with appropriate corrections for thermal expansion of the sample and for the temperature variation of refractive index of the ambient air. This method is one of the most accurate means in the determination of  $dn/dT$ , and hence

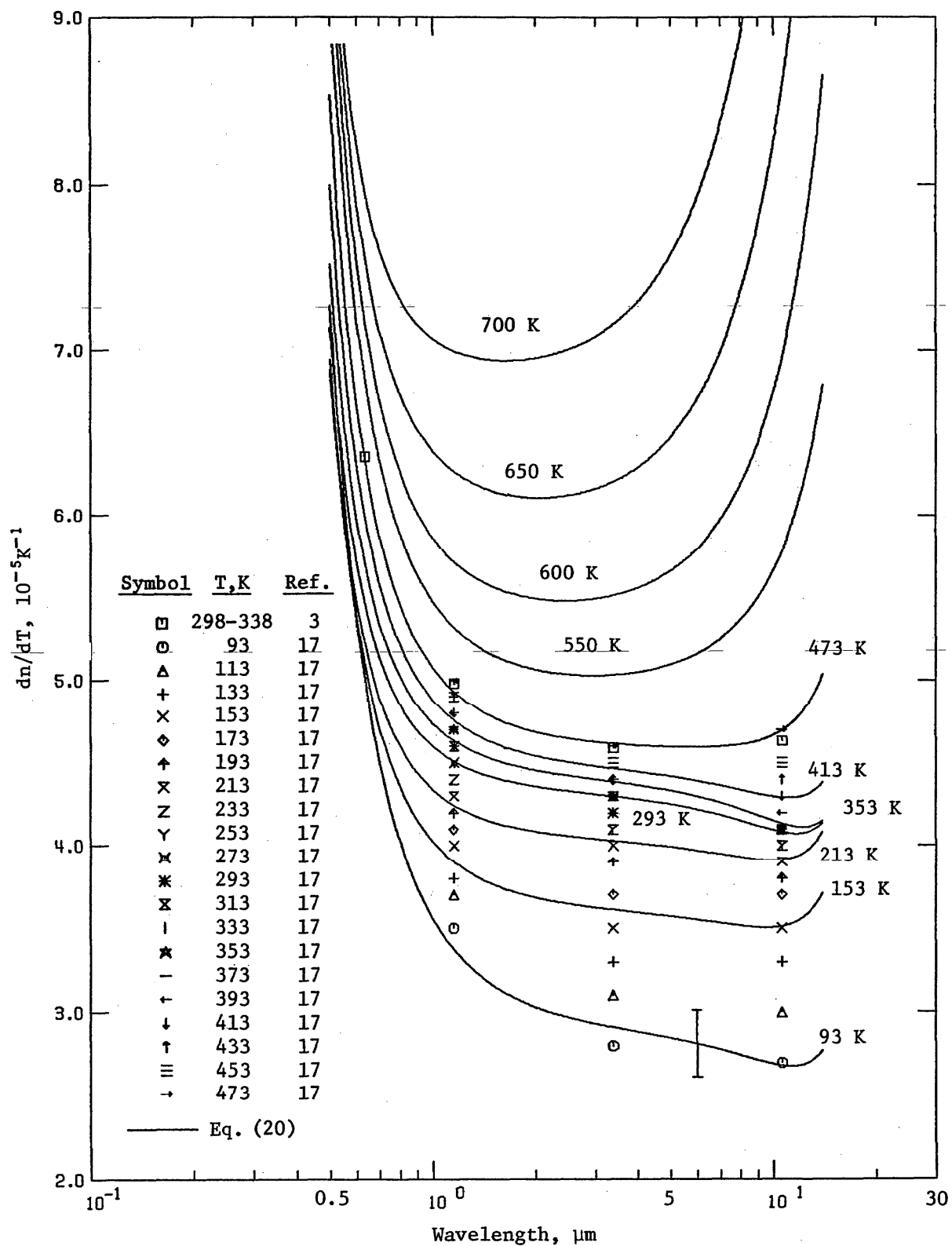


Figure 5. Experimental and calculated  $dn/dT$  of ZnS (wavelength dependence).

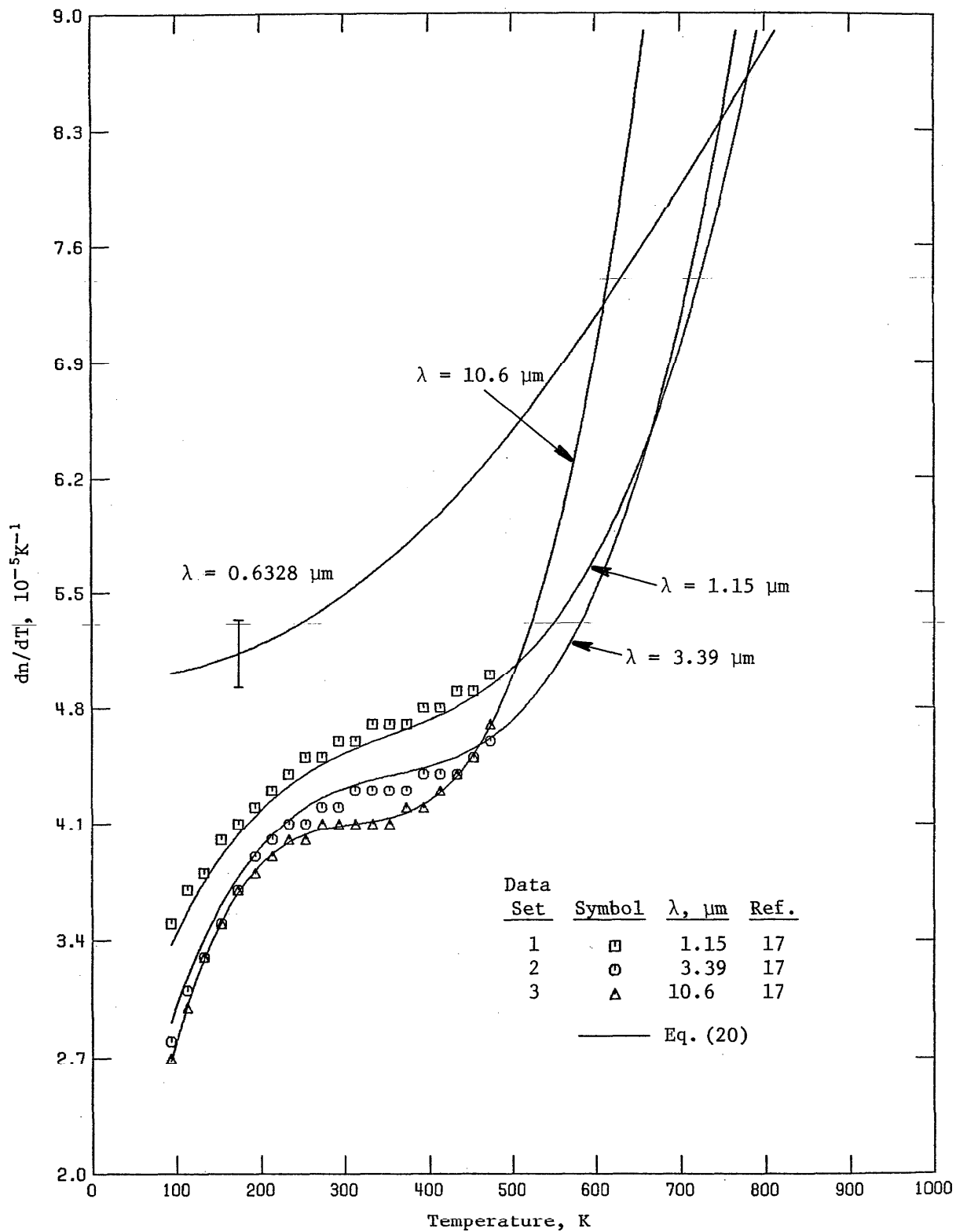


Figure 6. Experimental and calculated  $dn/dT$  of ZnS (temperature dependence).

the data are used as the basis of data analysis. Equation (18) should be used in the determination of the constants. However, there are problems which have to be clarified and solved before the calculation can be performed.

The first problem is the temperature variation of the parameters  $\lambda_u$  and  $\lambda_l$  in Eqs. (13) or (18). In the study of the fundamental optical absorption edge of a synthetic crystal of hexagonal zinc sulfide, Piper<sup>1</sup> found that the decreasing shift of band gap is approximately linearly proportional to temperature over a wide temperature range. In terms of wavelength shift, the corresponding proportionality constant is  $0.4841 \times 10^{-4} \mu\text{m K}^{-1}$ . This value is adopted for the parameter  $\beta_u$  because  $\lambda_u$ , though not exactly corresponding to the band gap, is the effective absorption band. The quoted shift is small and does not have much effect on the refractive index as a whole. We have, therefore,

$$\lambda_u = \lambda_{u0} + \beta_u t = 0.23979 + 0.484 \times 10^{-4} t,$$

where  $\lambda_{u0}$  is determined at room temperature as indicated in Eq. (19). Experimental values on the temperature dependence of  $\lambda_l$  are not available for ZnS but are available for ZnSe and ZnTe as measured by LaCombe and Irwin.<sup>6</sup> Since such shifts for compounds of the same family do not vary appreciably,<sup>5</sup> the experimental value of ZnSe,  $1/\lambda_l d\lambda_l/dT = 1.3 \times 10^{-4} \text{K}^{-1}$ , is adopted for ZnS. From that, the corre-

sponding value of  $\beta_l$ , i.e.,  $d\lambda_l/dT$ , of ZnS is  $0.00475 \mu\text{m K}^{-1}$  using  $\lambda_{l0} = 36.525$  determined at room temperature. The parameter  $\lambda_l$  is, therefore, expressible as  $\lambda_l = 36.525 + 0.00475 t$ .

The second problem is that the data of Feldman *et al.* is available only up to 473 K and only at three discrete wavelengths in the infrared. The constants based on these data may not be valid in the visible region and at higher temperatures. To check the validity of the results, data reported by Mell must agree with the predicted ones.

The third problem is the variation of  $dn/dT$  data with the temperature. In Fig. 6, one notices that in all three data sets,  $dn/dT$  increases monotonically with temperature from 93–300 K and remains essentially constant thereafter up to 400 K. After that the  $dn/dT$  appears to increase with temperature but there is no direct experimental data to support such behavior at higher temperatures. The same was also observed for ZnSe and it is reasonable to expect that both ZnS and ZnSe behave similarly. Evidence supporting the continuous increase of  $dn/dT$  versus temperature for ZnS at high temperatures is given for ZnSe by Mangir and Hellwarth.<sup>64</sup> They observed that within the experimental uncertainty,  $\pm 0.2 \times 10^{-5} \text{K}^{-1}$ , there is no variation of  $\Delta n/\Delta T$  values in the temperature range from 293 to 473 K but at higher temperatures up to 600 K there is a small constant

Table 3. Recommended values on the refractive index of CVD ZnS<sup>a</sup>

$\lambda, \mu\text{m}$	Temperature, K											
	93	143	193	243	293	343	393	443	493	543	593	618
0.50	2.4061	2.4096	2.4131	2.4165	2.4200	2.4236	2.4275	2.4315	2.4357	2.4402	2.4449	2.4473
0.55	2.3742	2.3773	2.3802	2.3832	2.3863	2.3895	2.3928	2.3963	2.3999	2.4038	2.4078	2.4099
0.60	2.3516	2.3543	2.3570	2.3597	2.3625	2.3654	2.3684	2.3716	2.3749	2.3784	2.3820	2.3839
0.65	2.3348	2.3373	2.3398	2.3424	2.3450	2.3477	2.3506	2.3535	2.3566	2.3598	2.3632	2.3650
0.70	2.3220	2.3243	2.3267	2.3292	2.3317	2.3343	2.3370	2.3398	2.3427	2.3457	2.3490	2.3507
0.75	2.3120	2.3142	2.3165	2.3188	2.3213	2.3238	2.3264	2.3291	2.3319	2.3348	2.3379	2.3395
0.80	2.3040	2.3061	2.3083	2.3106	2.3130	2.3154	2.3180	2.3206	2.3233	2.3261	2.3291	2.3307
0.85	2.2974	2.2994	2.3016	2.3039	2.3062	2.3086	2.3111	2.3137	2.3163	2.3191	2.3220	2.3236
0.90	2.2920	2.2940	2.2961	2.2983	2.3006	2.3030	2.3055	2.3080	2.3106	2.3133	2.3162	2.3177
0.95	2.2875	2.2894	2.2915	2.2937	2.2960	2.2983	2.3008	2.3032	2.3058	2.3085	2.3113	2.3128
1.0	2.2837	2.2856	2.2876	2.2898	2.2921	2.2944	2.2968	2.2992	2.3018	2.3044	2.3072	2.3087
1.5	2.2642	2.2659	2.2679	2.2700	2.2721	2.2744	2.2766	2.2789	2.2813	2.2838	2.2865	2.2879
2.0	2.2569	2.2586	2.2605	2.2626	2.2647	2.2669	2.2691	2.2714	2.2738	2.2762	2.2788	2.2802
2.5	2.2528	2.2545	2.2563	2.2584	2.2605	2.2627	2.2649	2.2672	2.2695	2.2719	2.2745	2.2759
3.0	2.2498	2.2514	2.2533	2.2553	2.2574	2.2596	2.2618	2.2641	2.2664	2.2688	2.2714	2.2728
3.5	2.2471	2.2487	2.2505	2.2526	2.2547	2.2569	2.2591	2.2613	2.2636	2.2660	2.2686	2.2700
4.0	2.2444	2.2460	2.2479	2.2499	2.2520	2.2542	2.2564	2.2586	2.2609	2.2633	2.2659	2.2673
4.5	2.2417	2.2433	2.2451	2.2471	2.2492	2.2514	2.2536	2.2558	2.2581	2.2605	2.2631	2.2645
5.0	2.2387	2.2403	2.2422	2.2442	2.2463	2.2484	2.2506	2.2528	2.2551	2.2575	2.2602	2.2616
5.5	2.2356	2.2371	2.2390	2.2410	2.2431	2.2452	2.2474	2.2496	2.2519	2.2543	2.2570	2.2584
6.0	2.2321	2.2337	2.2355	2.2375	2.2396	2.2418	2.2439	2.2461	2.2484	2.2508	2.2535	2.2550
6.5	2.2284	2.2300	2.2318	2.2338	2.2359	2.2380	2.2402	2.2424	2.2446	2.2471	2.2498	2.2513
7.0	2.2244	2.2260	2.2278	2.2298	2.2319	2.2340	2.2361	2.2383	2.2406	2.2431	2.2458	2.2473
7.5	2.2201	2.2216	2.2235	2.2254	2.2275	2.2296	2.2317	2.2339	2.2362	2.2387	2.2415	2.2430
8.0	2.2154	2.2169	2.2188	2.2207	2.2228	2.2249	2.2270	2.2292	2.2315	2.2340	2.2368	2.2384
8.5	2.2103	2.2119	2.2137	2.2157	2.2177	2.2198	2.2219	2.2241	2.2264	2.2289	2.2318	2.2334
9.0	2.2049	2.2064	2.2083	2.2102	2.2123	2.2143	2.2164	2.2186	2.2209	2.2235	2.2264	2.2280
9.5	2.1991	2.2006	2.2024	2.2044	2.2064	2.2085	2.2106	2.2127	2.2151	2.2176	2.2206	2.2223
10.0	2.1928	2.1944	2.1962	2.1981	2.2002	2.2022	2.2043	2.2065	2.2088	2.2114	2.2144	2.2161
10.5	2.1861	2.1876	2.1895	2.1914	2.1935	2.1955	2.1976	2.1997	2.2021	2.2047	2.2078	2.2095
11.0	2.1789	2.1805	2.1823	2.1843	2.1863	2.1883	2.1904	2.1926	2.1949	2.1976	2.2007	2.2025
11.5	2.1713	2.1728	2.1746	2.1766	2.1786	2.1807	2.1827	2.1849	2.1872	2.1899	2.1932	2.1950
12.0	2.1630	2.1646	2.1664	2.1684	2.1704	2.1725	2.1745	2.1767	2.1791	2.1818	2.1851	2.1871
12.5	2.1543	2.1558	2.1577	2.1597	2.1617	2.1637	2.1658	2.1680	2.1704	2.1732	2.1766	2.1786
13.0	2.1449	2.1465	2.1483	2.1503	2.1524	2.1544	2.1565	2.1587	2.1611	2.1639	2.1674	2.1695
13.5	2.1349	2.1365	2.1383	2.1404	2.1424	2.1445	2.1466	2.1488	2.1512	2.1541	2.1577	2.1599
14.0	2.1242	2.1258	2.1277	2.1297	2.1318	2.1339	2.1360	2.1382	2.1407	2.1436	2.1474	2.1496

<sup>a</sup> In the wavelength region between 0.50 and 1.0  $\mu\text{m}$ , the values are also for natural ZnS but with higher uncertainties as discussed in the text. At room temperature, the valid wavelength range for natural ZnS is from 0.50 to 2.4  $\mu\text{m}$ .



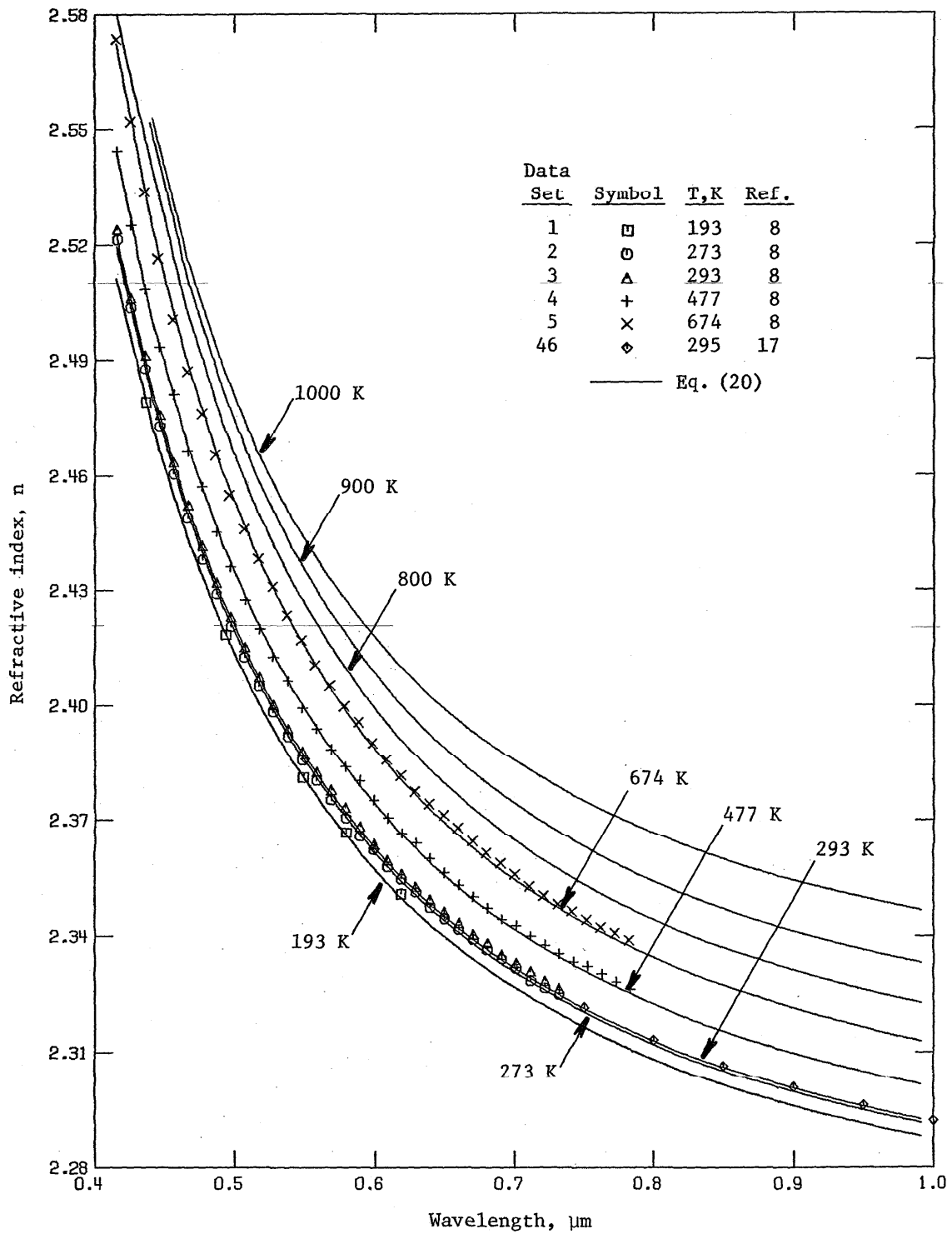


Figure 7. Comparison of experimental and calculated refractive indices of ZnS at various temperatures.

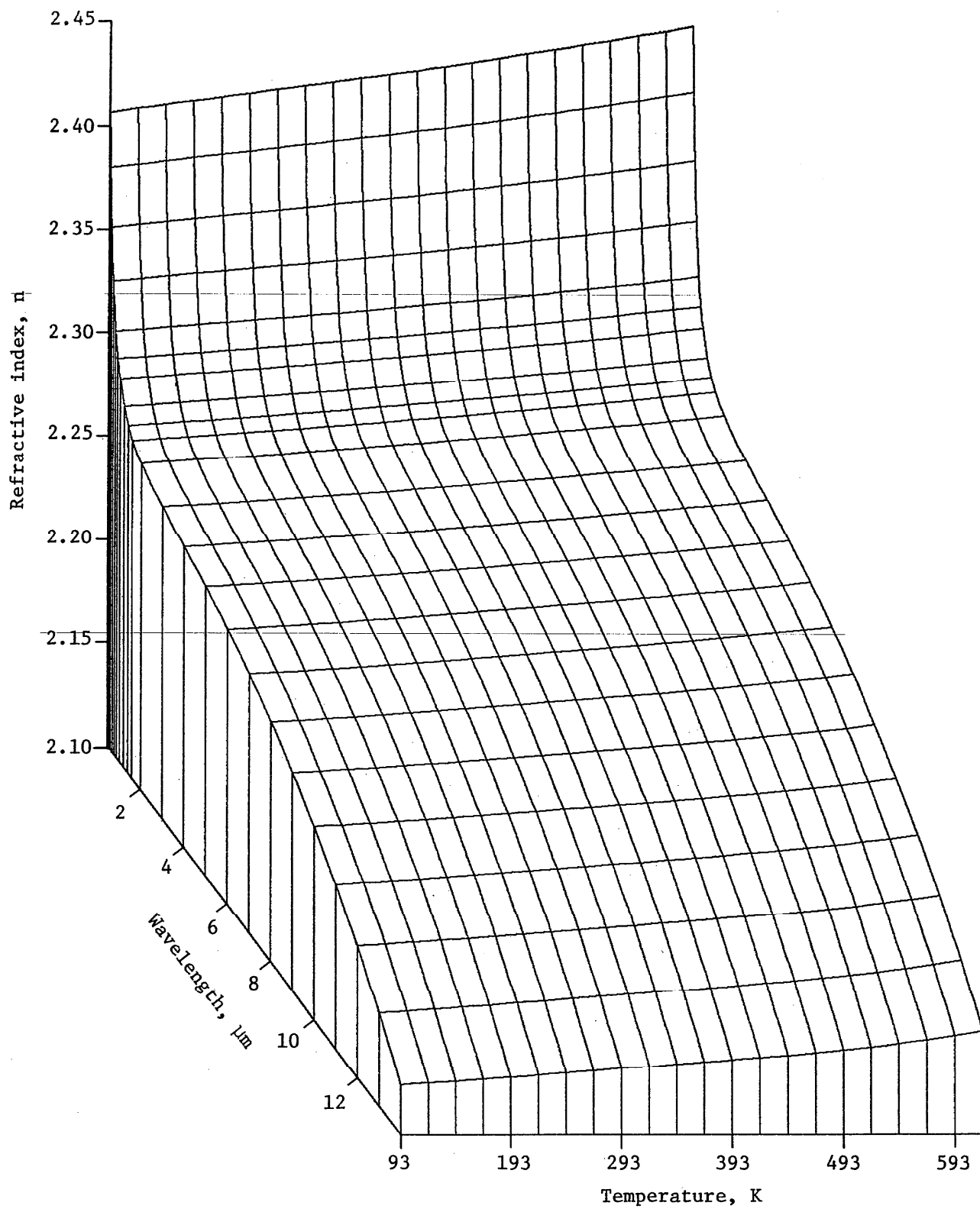


Figure 8. Recommended  $n$ - $\lambda$ - $T$  diagram of ZnS.

increase at a rate of  $0.5 \times 10^{-5}$  per 100 K at all wavelengths. Additional evidence was found by Mell; at wavelengths 0.578 and 0.619  $\mu\text{m}$  the  $\Delta n/\Delta T$  values are found to be increasing with temperature at a rate of about  $0.4\text{--}0.6 \times 10^{-5}$  per 100 K in the temperature range from 477 to 979 K. All of the evidence suggests that the  $dn/dT$  of ZnS is continuously increasing with temperature in the temperature range above 475 K.

With all these considerations, a least-squares fit of  $dn/dT$  data to Eq. (18) gives the following expression for the refractive index of ZnS as a function of both wavelength and temperature:

$$n^2(\lambda, t) = E(t) + \frac{A(t)}{\lambda^2 - \lambda_u^2} + \frac{B(t)}{\lambda^2/\lambda_l^2 - 1}, \quad (20)$$

where  $\lambda$  is in units of  $\mu\text{m}$ ,

$t = T - 293$  in units of K,

$\lambda_u = 0.23979 + 4.841 \times 10^{-5}t$  in units of  $\mu\text{m}$ ,

$\lambda_l = 36.525 + 4.75 \times 10^{-3}t$  in units of  $\mu\text{m}$ ,

$E(t) = 8.34096 + 1.29107 \times 10^{-3}t + 4.68388 \times 10^{-7}t^2$   
 $- 1.31683 \times 10^{-9}t^3 - 6.64356 \times 10^{-12}t^4$ ,

$A(t) = 0.14540 + 1.13319 \times 10^{-5}t + 1.05932 \times 10^{-8}t^2$   
 $+ 1.06004 \times 10^{-10}t^3 - 2.27671 \times 10^{-13}t^4$ ,

and

$$B(t) = 3.23924 + 1.09600 \times 10^{-3}t + 4.20092 \times 10^{-7}t^2$$

$$- 1.11350 \times 10^{-9}t^3 - 7.2992 \times 10^{-12}t^4.$$

It should be pointed out that this equation is based on essentially the data of Mell and Feldman *et al.* and is, therefore, valid for both CVD ZnS and natural ZnS. Since the parameters  $\lambda_{10}$ ,  $\beta_u$ ,  $\beta_l$ ,  $\epsilon_\infty$ , and  $\epsilon_0$  are those of pure crystal samples, it is expected that this equation is also valid for the pure crystal. At present, however, not enough data for crystals are available to substantiate this.

Equation (20) is used to generate the recommended values of the refractive index of CVD ZnS and natural ZnS given in Table 3 and plotted in Figs. 7 and 8. A comparison of calculated values with the experimental data for a few specified temperatures and wavelengths are plotted in Figs. 2 and 7 where excellent agreement is observed. Table 4 gives the calculated  $dn/dT$  values for CVD ZnS based on the first derivative of Eq. (20) with respect to  $T$  with the corresponding curves shown in Fig. 9. Calculated room temperature  $dn/d\lambda$  values for CVD ZnS based on the first derivative of Eq. (20) with respect to  $\lambda$  at 293 K are given in Table 5 and shown in Fig. 10.

For CVD ZnS, Eq. (20) is valid over a wavelength range from 0.5 to 14  $\mu\text{m}$  and a temperature range from 93 up to 618

Table 4. Recommended values (in units of  $10^{-5}\text{K}^{-1}$ ) on the temperature derivative of refractive index of CVD ZnS<sup>a</sup>

$\lambda$ , $\mu\text{m}$	Temperature, K											
	93	143	193	243	293	343	393	443	493	543	593	618
0.50	7.3	7.0	6.9	6.9	7.1	7.4	7.8	8.3	8.7	9.1	9.5	9.7
0.55	6.1	6.0	6.0	6.1	6.2	6.5	6.8	7.1	7.5	7.9	8.2	8.4
0.60	5.4	5.4	5.4	5.5	5.7	5.9	6.2	6.5	6.8	7.1	7.5	7.6
0.65	4.9	5.0	5.1	5.2	5.4	5.5	5.8	6.0	6.3	6.6	7.0	7.2
0.70	4.5	4.7	4.8	5.0	5.1	5.3	5.5	5.7	6.0	6.3	6.6	6.8
0.75	4.2	4.5	4.7	4.8	5.0	5.1	5.3	5.5	5.7	6.0	6.4	6.6
0.80	4.0	4.3	4.5	4.7	4.8	5.0	5.1	5.3	5.6	5.8	6.2	6.4
0.85	3.9	4.2	4.4	4.6	4.8	4.9	5.0	5.2	5.4	5.7	6.1	6.3
0.90	3.7	4.1	4.4	4.5	4.7	4.8	4.9	5.1	5.3	5.6	6.0	6.2
0.95	3.6	4.0	4.3	4.5	4.6	4.8	4.9	5.0	5.2	5.5	5.9	6.1
1.0	3.6	4.0	4.2	4.5	4.6	4.7	4.8	5.0	5.2	5.4	5.8	6.0
1.5	3.2	3.7	4.0	4.3	4.4	4.5	4.6	4.7	4.8	5.1	5.5	5.8
2.0	3.0	3.6	4.0	4.2	4.4	4.4	4.5	4.6	4.8	5.0	5.4	5.7
2.5	3.0	3.6	3.9	4.2	4.3	4.4	4.5	4.6	4.7	5.0	5.4	5.7
3.0	2.9	3.5	3.9	4.2	4.3	4.4	4.5	4.5	4.7	5.0	5.4	5.7
3.5	2.9	3.5	3.9	4.2	4.3	4.4	4.4	4.5	4.7	5.0	5.4	5.7
4.0	2.9	3.5	3.9	4.1	4.3	4.4	4.4	4.5	4.7	5.0	5.5	5.8
4.5	2.9	3.5	3.9	4.1	4.3	4.3	4.4	4.5	4.7	5.0	5.5	5.9
5.0	2.8	3.5	3.9	4.1	4.3	4.3	4.4	4.5	4.7	5.0	5.6	5.9
5.5	2.8	3.5	3.9	4.1	4.2	4.3	4.4	4.5	4.7	5.1	5.6	6.0
6.0	2.8	3.5	3.9	4.1	4.2	4.3	4.4	4.5	4.7	5.1	5.7	6.1
6.5	2.8	3.4	3.8	4.1	4.2	4.3	4.3	4.5	4.7	5.1	5.8	6.2
7.0	2.8	3.4	3.8	4.1	4.2	4.2	4.3	4.5	4.7	5.2	5.9	6.3
7.5	2.8	3.4	3.8	4.1	4.2	4.2	4.3	4.5	4.7	5.2	5.9	6.4
8.0	2.7	3.4	3.8	4.0	4.2	4.2	4.3	4.4	4.8	5.3	6.1	6.6
8.5	2.7	3.4	3.8	4.0	4.1	4.2	4.3	4.4	4.8	5.3	6.2	6.7
9.0	2.7	3.4	3.8	4.0	4.1	4.2	4.3	4.4	4.8	5.4	6.3	6.9
9.5	2.7	3.4	3.8	4.0	4.1	4.2	4.2	4.4	4.8	5.5	6.4	7.0
10.0	2.7	3.4	3.8	4.0	4.1	4.1	4.2	4.4	4.9	5.5	6.6	7.2
10.5	2.7	3.4	3.8	4.0	4.1	4.1	4.2	4.5	4.9	5.6	6.7	7.4
11.0	2.7	3.4	3.8	4.0	4.1	4.1	4.2	4.5	4.9	5.7	6.9	7.7
11.5	2.7	3.4	3.8	4.0	4.1	4.1	4.2	4.5	5.0	5.8	7.1	7.9
12.0	2.7	3.4	3.9	4.0	4.1	4.1	4.2	4.5	5.0	6.0	7.3	8.2
12.5	2.7	3.5	3.9	4.0	4.1	4.1	4.2	4.5	5.1	6.1	7.5	8.5
13.0	2.7	3.5	3.9	4.1	4.1	4.1	4.2	4.6	5.2	6.2	7.8	8.8
13.5	2.7	3.5	4.0	4.1	4.1	4.1	4.2	4.6	5.3	6.4	8.1	9.1
14.0	2.8	3.6	4.0	4.1	4.1	4.1	4.3	4.6	5.4	6.6	8.4	9.5

<sup>a</sup>In the wavelength region between 0.50 and 1.0  $\mu\text{m}$ , the values are also for natural ZnS.

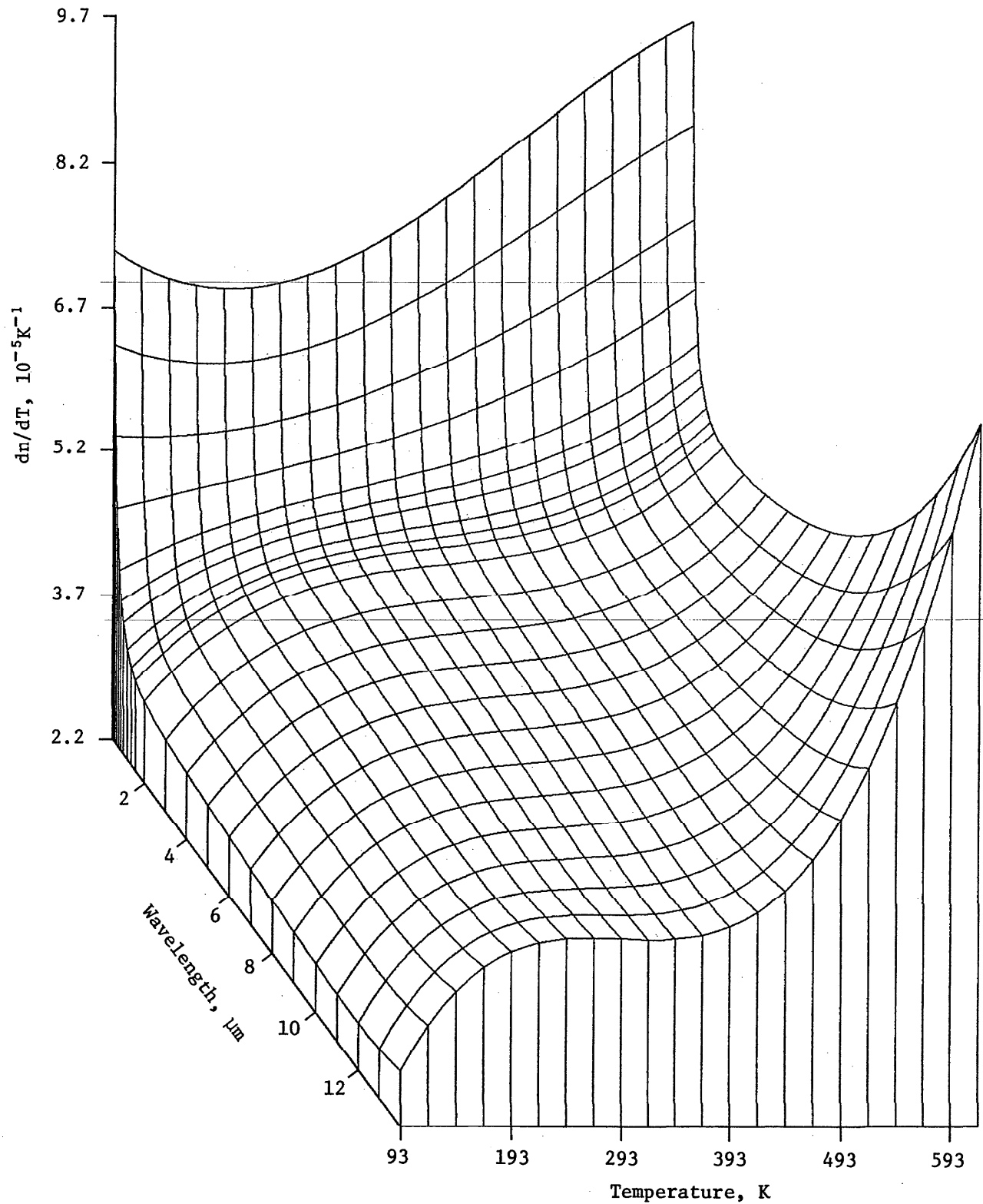


Figure 9. Recommended  $dn/dT$ - $\lambda$ - $T$  diagram of ZnS.

Table 5. Recommended values on the wavelength derivative of refractive index of CVD ZnS

$\lambda$ , $\mu\text{m}$	$-\frac{dn}{d\lambda}$ , $10^{-3}\mu\text{m}^{-1}$
0.50	811.2 <sup>a</sup>
0.55	558.9
0.60	404.2
0.65	303.2
0.70	234.1
0.75	185.0
0.80	149.1
0.85	122.1
0.90	101.4
0.95	85.3
1.0	72.5
1.5	21.6
2.0	10.4
2.5	6.9
3.0	5.7
3.5	5.4
3.6 <sup>b</sup>	5.35 <sup>b</sup>
4.0	5.4
4.5	5.7
5.0	6.1
5.5	6.6
6.0	7.2
6.5	7.8
7.0	8.4
7.5	9.1
8.0	9.8
8.5	10.5
9.0	11.3
9.5	12.1
10.0	13.0
10.5	13.9
11.0	14.8
11.5	15.8
12.0	16.9
12.5	18.0
13.0	19.3
13.5	20.6
14.0	21.9

<sup>a</sup>The uncertainties of  $dn/d\lambda$  (in units of  $10^{-3}\mu\text{m}^{-1}$ ) are:  $\pm 5$  at  $0.5\mu\text{m}$ ,  $\pm 4$  at  $0.6\mu\text{m}$ ,  $\pm 2$  at  $1\mu\text{m}$ ,  $\pm 0.4$  at  $5\mu\text{m}$ ,  $\pm 0.2$  at  $10\mu\text{m}$ , and  $\pm 0.2$  at  $14\mu\text{m}$ .

<sup>b</sup>Minimum point on the curve.

K based entirely on the available data and supporting evidence as discussed earlier and appropriate extrapolation from 600 to 618 K. Extrapolation beyond 618 K is not recommended as the temperature-dependent terms are determined by empirical fit of limited available data without real physical meaning. Although outstanding agreement between Mell's data and the predicted values at high temperatures (Figs. 2 and 7) encourages extrapolation, the predicted rate of increase for  $dn/dT$  at high temperatures for infrared wavelengths (see Fig. 6) precludes accurate extrapolation. For natural crystal ZnS, Eq. (20) is valid over the narrow wavelength region between 0.5 to  $1\mu\text{m}$  and over a wider temperature range from 93 to 1000 K. The valid wavelengths are limited to that narrow region because refractive index data of natural ZnS are available only in the visible region and there is no reliable data beyond  $1\mu\text{m}$ .

Uncertainties of the recommended refractive index are estimated based on the standard deviations of data fit calculations and/or by comparison to the available data. For CVD ZnS in the recommended temperature region, the estimated uncertainties are  $\pm 0.0003$  in wavelength region between 0.6 and  $11\mu\text{m}$ ,  $\pm 0.0005$  between 0.5 to  $0.6\mu\text{m}$ , and  $\pm 0.001$  between 11 and  $14\mu\text{m}$ . For natural ZnS in the wavelength region between 0.5 and  $1.0\mu\text{m}$ , the uncertainty

of  $\pm 0.002$  is applied in the temperature region  $\leq 618\text{ K}$ , beyond which large uncertainties are expected.

Estimation of uncertainties in the recommended  $dn/dT$  values are based on the results of Feldman *et al.* which are used to determine the constants of Eq. (20). Their reported experimental uncertainties are  $\pm 0.2 \times 10^{-5}\text{K}^{-1}$  for all the three wavelengths investigated. Our least-squares calculations yielded basically the same uncertainties. Error bars corresponding to this value are indicated in Figs. 5 and 6 where calculations are compared with the experimental data.

Uncertainties of the recommended  $dn/d\lambda$  values can be estimated in the following manner. Taking the first derivative of Eq. (19) with respect to  $\lambda$ , we have

$$-(n/\lambda)(dn/d\lambda) = A_0R_u^2 + B_0R_l^2/\lambda_l^2$$

which leads to

$$\delta\left(\frac{dn}{d\lambda}\right) = \frac{\lambda\delta n}{n^2} \left( A_0R_u^2 + \frac{B_0R_l^2}{\lambda_l^2} + 4n^2R_u + \frac{4n^2|R_l|}{\lambda_l^2} \right). \quad (21)$$

Based on the quoted uncertainties for refractive index of CVD ZnS, it is appropriate to adopt  $\delta n = \pm 0.0005$  for the evaluation of  $\delta(dn/d\lambda)$  for the entire wavelength range from 0.5 to  $14\mu\text{m}$ .

### 3.2. Zinc Selenide, ZnSe

There are 36 sets of experimental data available for the refractive index (wavelength dependence and temperature dependence) of zinc selenide as plotted in Figs. 11 and 12. Some of the data sets are for thin films or multiple layers, included here for the purpose of comparison and completeness. Several of the data sets were eliminated from further consideration because of inadequate specimen characterization or unreliable techniques. The data sets reported by Marple,<sup>48,49</sup> Rambauske,<sup>50,51</sup> Hilton and Jones,<sup>52</sup> Wunderlich and DeShazer,<sup>53</sup> Feldman *et al.*,<sup>17</sup> and Thompson *et al.*<sup>54</sup> are considered most representative of the available refractive index for zinc selenide in the fundamental transparent region between 0.4 and  $18.2\mu\text{m}$ ; while data sets reported by Hattori *et al.*<sup>19</sup> are the only available data in the wavelength range from 83 to  $1163\mu\text{m}$ . The data reported by Manabe *et al.*<sup>16</sup> and Hadni *et al.*<sup>55,56</sup> concern the characteristics of the reststrahlen region; and the data of Aven *et al.*<sup>57</sup> are for both the reststrahlen and electronic absorption regions.

#### 3.2.1. Review of Available Data

For the purpose of obtaining a consistent refractive index of ZnSe over a wavelength range from the short-wave transmission limit set by the band gap to  $2.5\mu\text{m}$ , Marple<sup>48,49</sup> carefully measured the refractive index of ZnSe prisms with impurities less than 10–20 ppm. Experimental error of the data is reported as  $\pm 0.002$  or less; however, the results for two ZnSe prisms differ by up to 0.005 in the wavelength region between 0.496 and  $0.83\mu\text{m}$ . The cause of this difference is unknown and cannot be accounted for by the error in the prism angle measurements alone. One possible cause is the impurity content or stoichiometric balance between the prisms. One showed a slightly brownish tint compared with

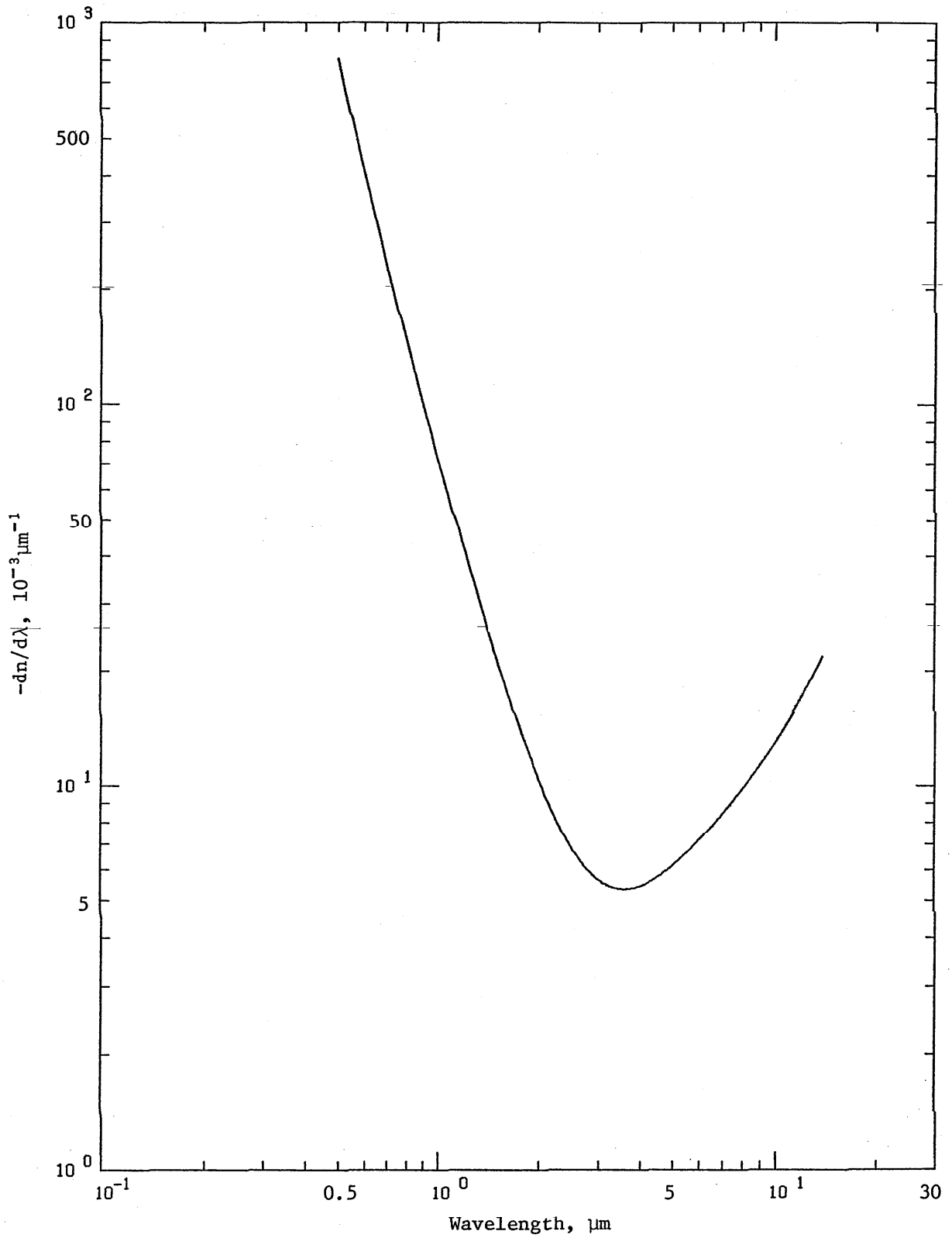


Figure 10. Recommended  $dn/d\lambda$  curve of ZnS at 293 K.

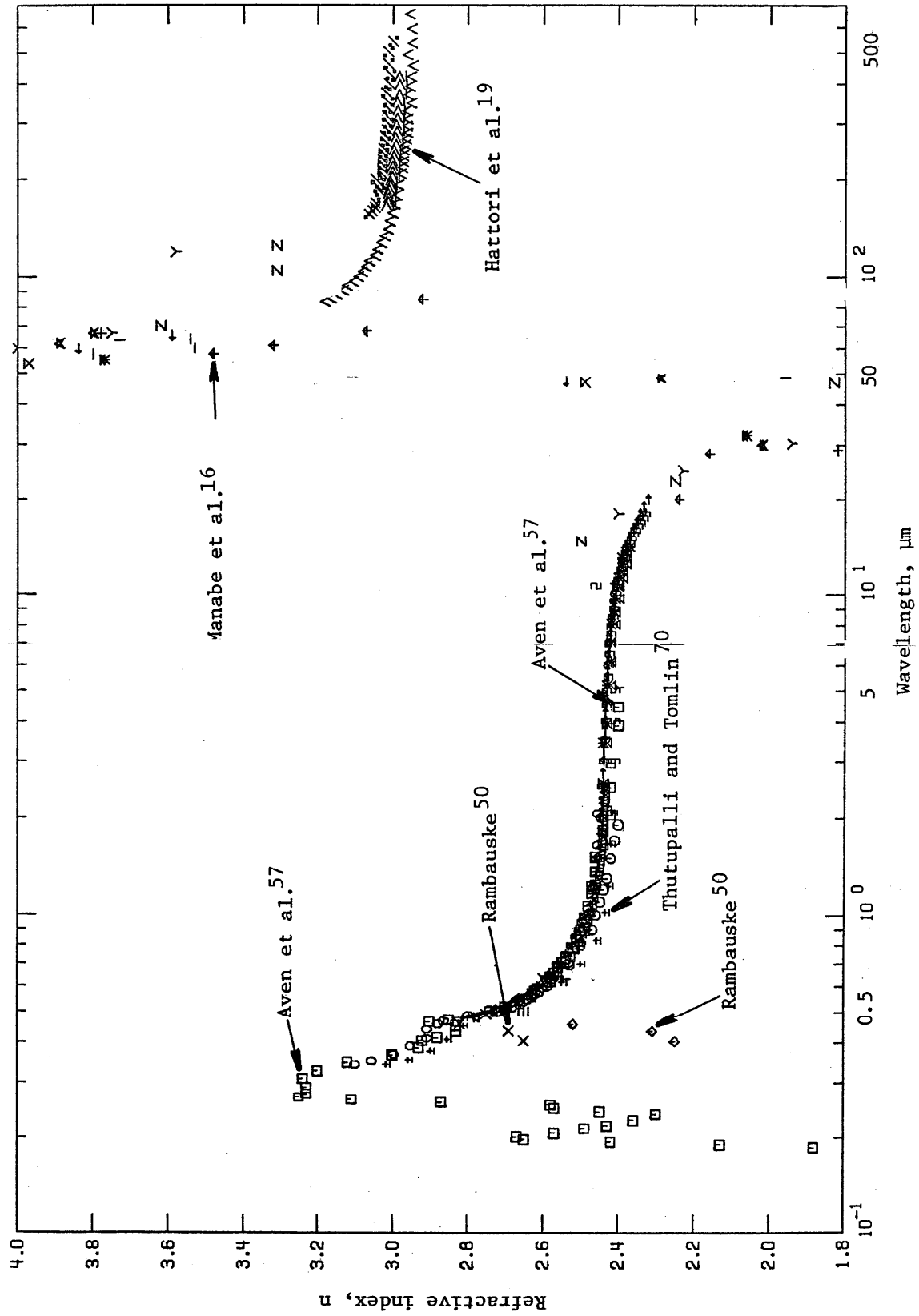


Figure 11. Available experimental refractive index of ZnSe (wavelength dependence).

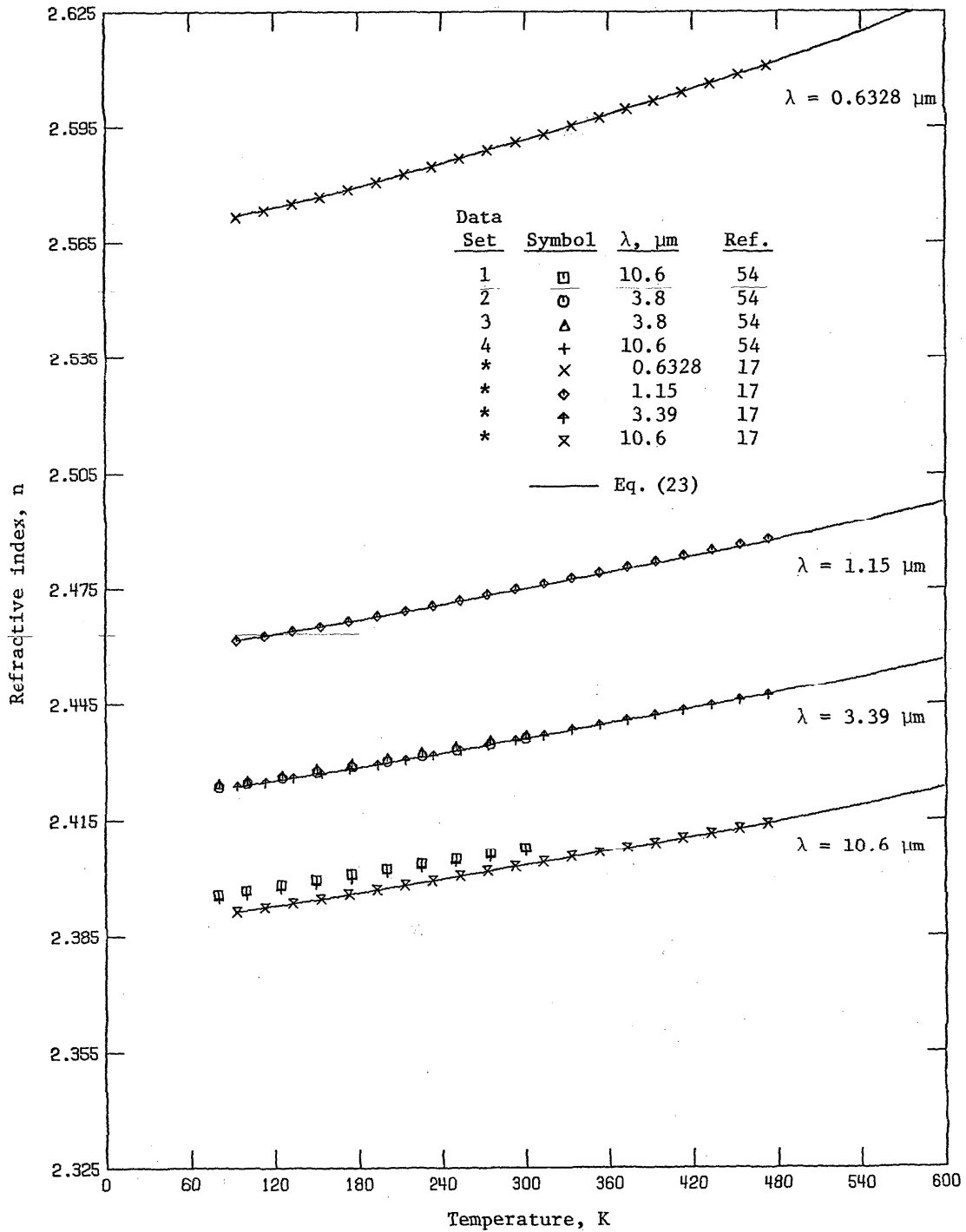


Figure 12. Experimental and calculated refractive index of ZnSe (temperature dependence).



Table 6. Comparison of dispersion equations proposed for ZnSe

Source	Wavelength and temperature ranges	Dispersion equation $\lambda$ in $\mu\text{m}$ , $\Omega = \lambda/\lambda_I$
Marple, D.T.F., 1964; Ref. 48	0.48-2.50 $\mu\text{m}$ 298 K	for one sample: $n^2 = 4.00 + \frac{1.90 \lambda^2}{\lambda^2 - 0.113}$ for second sample: $n^2 = 3.71 + \frac{2.19 \lambda^2}{\lambda^2 - 0.105}$
Manabe, A., Mitsubishi, A., and Yoshinaga, H., 1967; Ref. 16	20-85 $\mu\text{m}$ 300 K 100 K	$n^2 - k^2 = \epsilon_\infty + \frac{N(1-\Omega^2)}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ $2nk = \frac{N\delta\Omega}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ at 300 K: $\epsilon_\infty = 5.4$ , $\lambda_I = 48.31$ , $\delta = 0.018$ , and $N = 2.2$ ; at 100 K: $\epsilon_\infty = 5.4$ , $\lambda_I = 47.39$ , $\delta = 0.010$ , and $N = 2.2$ .
Handi, A., Henry, P., Lambert, J.P., Morlot, G., Strimer, P., and Chanal, D., 1967; Ref. 55	15-125 $\mu\text{m}$ 290 K 90 K	$n^2 - k^2 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)(1-\Omega^2)}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ $2nk = \frac{(\epsilon_0 - \epsilon_\infty)\delta\Omega}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ at 290 K: $\epsilon_\infty = 6.3$ , $\epsilon_0 = 9.6$ , $\lambda_I = 49.0$ , and $\delta = 0.022$ ; at 90 K: $\epsilon_\infty = 6.3$ , $\epsilon_0 = 9.53$ , $\lambda_I = 47.44$ , and $\delta = 0.010$ .
Handi, A., et al., 1967; Ref. 55, cont.		
Kodak publication U-72, 1971; Ref. 21	1.0-20 $\mu\text{m}$ 300-K	$n = 2.4350823 + \frac{5.1567472 \times 10^{-2}}{\lambda^2 - 0.028} + \frac{2.4901923 \times 10^{-3}}{(\lambda^2 - 0.028)^2} - 2.7245212 \times 10^{-8}\lambda^2 - 9.8541275 \times 10^{-8}\lambda^4$
Hattori, T., Homma, Y., Mitsubishi, A., and Tacke, M., 1973; Ref. 19	156-541 $\mu\text{m}$ at 300 K 166-422 $\mu\text{m}$ at 80 K 83-1163 $\mu\text{m}$ at 2 K	$n^2 = \frac{\epsilon_0 - \epsilon_\infty\Omega^2}{1 - \Omega^2}$ at 300 K: $\epsilon_0 = 8.99$ , $\epsilon_\infty = 5.3$ , and $\lambda_I = 49.261 \mu\text{m}$ ; at 80 K: $\epsilon_0 = 8.76$ , $\epsilon_\infty = 5.5$ , and $\lambda_I = 48.309 \mu\text{m}$ ; at 2 K: $\epsilon_0 = 8.68$ , $\epsilon_\infty = 5.6$ , and $\lambda_I = 47.619 \mu\text{m}$ .
Wunderlich, J.A. and DeShazer, L.G., 1977; Ref. 53	0.5017-0.6328 $\mu\text{m}$ 300 K	$n^2 = 1 + \frac{4.7032 \lambda^2}{\lambda^2 - (0.26522)^2}$
Feldman, A., Horowitz, D., Waxler, R.M., and Dodge, M.J., 1978; Ref. 17	0.54-18.2 $\mu\text{m}$ 293 K	$n^2 = 1 + \frac{3}{\Sigma} \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}$ for one sample at 293.3 K: $A_1 = 4.2980149$ $A_2 = 0.62776557$ $A_3 = 2.8955633$ $\lambda_1 = 0.19206300$ $\lambda_2 = 0.37878260$ $\lambda_3 = 46.994595$ for second sample at 293.8 K: $A_1 = 4.4639521$ $A_2 = 0.46132463$ $A_3 = 2.8828867$ $\lambda_1 = 0.20107634$ $\lambda_2 = 0.39210520$ $\lambda_3 = 47.047590$
Present work, 1982	0.55-18 $\mu\text{m}$ 93-618 K	$n^2(\lambda, t) = E(t) + \frac{A(t)}{\lambda^2 - \lambda_u^2} + \frac{B(t)}{\lambda^2/\lambda_I^2 - 1}$ $t = T - 293$ See Eq. (23) in text for the expressions of $\lambda_u$ , $\lambda_I$ , $E(t)$ , $A(t)$ , and $B(t)$ .

Table 7. Available data on  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_T$  of ZnSe

Temp., K	$\epsilon_\infty$	$\epsilon_0$	$\lambda_T, \mu\text{m}$	Ref.
300	5.4	7.6	48.31, 49.02	16
300		9.12		24
300	5.90			48
300			49.26	58
300	5.3	8.99	49.26	19
300	$5.75 \pm 0.1$	$8.1 \pm 0.3$	47.69	57
300	6.3	9.6	49.02, 48.97	56
300	5.4	7.6	48.31	59
300	6.10	9.2	47.85	60
300			46.51	27
300			49.02	61
300	5.86			21
300	6.3			50
80	5.5	8.76	48.31	19
80	6.3	9.53	47.44	56
80	5.4	7.6	47.39	59
80	5.4	7.6	47.39	16
2	5.6	8.68	47.62	19

the lemon-yellow color of the purer ZnSe sample. As shown in Table 7, the equation  $n^2 = A + B\lambda^2/(\lambda^2 - C^2)$  was used to fit experimental data for each prism with  $A$ ,  $B$ , and  $C$  being adjustable. Because of the limited spectral range,  $A$ ,  $B$ , and  $C$  were not determined with a more realistic theory of the dielectric constants. However, the best-fit values of  $A$ ,  $B$ , and  $C$  for each of the two prisms indicate a value of 5.90 for the optical dielectric constant of ZnSe.

Rambauske<sup>50,51</sup> reported refractive index data over a spectral range from 0.400 to 0.644  $\mu\text{m}$  for two ZnSe specimens obtained from different suppliers. The orange-yellow specimen from Aerospace Research Laboratory was of high purity and the results for which are more representative of pure ZnSe; the yellow specimen from Harshaw Chemical Co. contained considerable impurities and the results for which are quite discrepant from the former. Although the size of discrepancy in the transparent region is less than one unit in the second decimal place, it is significantly larger in the absorption region. For example, the refractive index of Harshaw specimen is 2.25 at 0.4044  $\mu\text{m}$  and 2.65 for other specimens. Additional data in the visible region between 0.50 and 0.633  $\mu\text{m}$  were reported by Wunderlich and De-Shazer.<sup>53</sup> The minimum deviation method was used and experimental error in  $n$  was reported to be  $\pm 0.002$ . The data were fitted to a single term Sellmeier formula as given in Table 6.

In an effort to measure the refractive index of polycrystalline ZnSe with high precision, Hilton and Jones<sup>52</sup> reported data for an Irtran 4 specimen over a wavelength range from 2.5 to 14  $\mu\text{m}$  at two temperatures, 295 and 198 K, using minimum deviation method. Based on the data obtained at these temperatures, the average temperature coefficient of refractive index at 5  $\mu\text{m}$  was evaluated to be  $4.8 \times 10^{-5} \text{K}^{-1}$ , comparable with those reported in other studies.

The refractive index of CVD ZnSe were measured by

Feldman *et al.*<sup>17</sup> as part of the effort in the characterization of high-power laser window materials. Two CVD ZnSe samples were measured with high-precision minimum deviation method over a wide wavelength range of laser interest from 0.54 to 18.2  $\mu\text{m}$ . The reported room-temperature data were given to the fifth decimal place and were fitted to a three-term Sellmeier-type dispersion equation (Table 6). Since the parameters in their dispersion equation were not intended to have physical significance but are a mathematical fit the values for these two samples are considerably different even though the difference in refractive indices at any wavelength is less than four units in the fourth decimal place. In view of the reported average absolute residuals of  $n$  from the best-fit equation of each data set,  $6.2 \times 10^{-5}$  and  $4.1 \times 10^{-5}$ , respectively, the difference of four units in the fourth decimal place cannot be accounted for by experimental errors. The discrepancies in these two data sets might be due to impurities or crystal defects. An uncertainty of magnitude  $\pm 0.0004$  will be a reasonable estimate for reference data values.

The indices of refraction of ZnSe in the far infrared spectral range from 83 to 1163  $\mu\text{m}$  were measured by Hattori *et al.*<sup>19</sup> at temperatures of 2, 80, and 300 K. The results are described by a simple dispersion equation (Table 6) for an undamped harmonic oscillator from which the static dielectric constant, optical dielectric constant, and wavelength of TO mode phonon were determined with least-squares fit. The static dielectric constant serves as a check for the values obtained from various optical methods. Since the data were measured by an interference method, the value of  $\epsilon_0$ , obtained in the long wavelength region, is believed to be reliable and should be adopted as a known parameter in the dispersion equation of ZnSe.

Manabe *et al.*<sup>16</sup> studied optical constants in the reststrahlen region by means of infrared lattice reflection spectra in the spectral region between 20 and 85  $\mu\text{m}$  using the Drude dispersion relation. The oscillator strength  $N$ , optical dielectric constant  $\epsilon_\infty$ , damping factor  $\delta$ , and wavelength of transverse optical phonon  $\lambda_T$ , in the Drude equations (Table 6) were determined by fit of reflectivity data. The wavelength of transverse optical phonon was also determined directly from transmission measurements on an evaporated thin film and was found to agree with that obtained from the reflection spectra analysis. The static dielectric constant  $\epsilon_0$  was determined by letting  $\lambda = \infty$  in the resulting Drude equation assuming zero absorption, i.e.,  $\epsilon_0 = n^2 = \epsilon_\infty = N\lambda_T^2$ . Optical constants in the reststrahlen region were also studied by Hadni *et al.*<sup>55,56</sup> for an Irtran 4 sample at temperatures 80 and 290 K. The various parameters,  $\epsilon_0$ ,  $\epsilon_\infty$ , and  $\lambda_T$ , were determined from analyzing the reflection and transmission spectra with the Kramers-Kronig relations and with the Lorentz one-oscillator model. Aven *et al.*<sup>57</sup> performed a similar study on a single crystal of ZnSe to determine the wavelength of an optical phonon and optical dielectric constants. The static dielectric constant was determined from capacitance measurements on a single-crystal wafer. In addition, the absorption bands in the ultraviolet region were also observed. The wavelengths of the absorption bands were determined at 0.459, 0.394, 0.261, and 0.243  $\mu\text{m}$  with the first one corresponding to the energy gap.

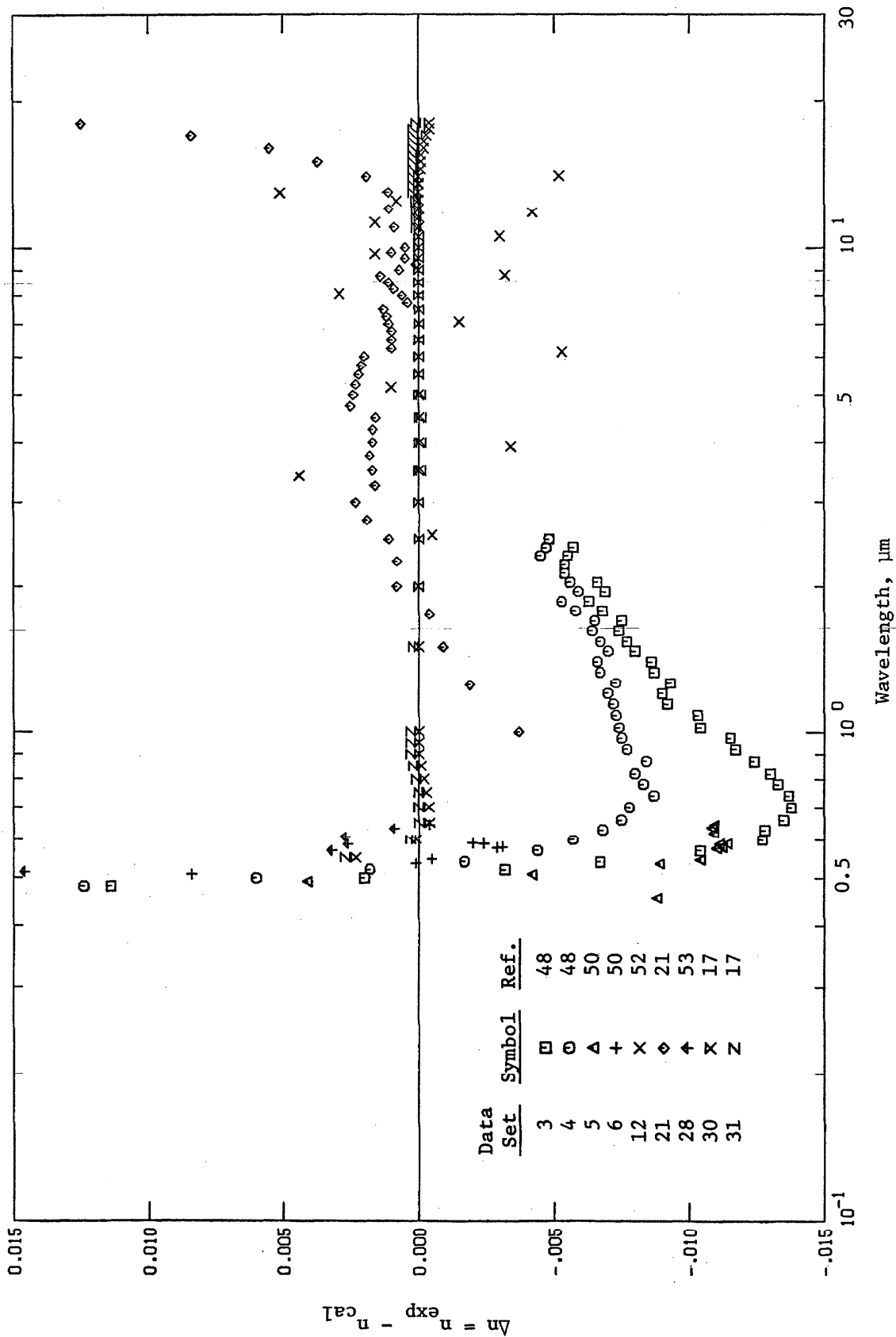


Figure 13. Comparison of experimental and calculated refractive index values of ZnSe at room temperature. The calculated values from Eq. (22) are represented by the line  $\Delta n = 0$

For ease of comparison, the above mentioned data sets for the fundamental transparent region are plotted in Fig. 13. It is obvious that the disagreement among the data sets reported by different investigators is greater than the accuracy claimed by each of them. Although internal consistency was observed in each investigation, unaccounted sources of errors are responsible for these discrepancies.

### 3.2.2. Room-Temperature Dispersion Equation

In the present work, Eq. (9) is used to represent the room-temperature refractive index of ZnSe. The main problems are to select the appropriate parameters,  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_1$ , and to determine the coefficients  $A$ ,  $B$ , and the parameters  $\lambda_u$ . Literature values of  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_1$  are very discrepant as shown in Table 7. The available room-temperature  $\epsilon_\infty$  values vary from 5.3 to 6.3. This variation is far too great for refractive index calculations; one has to resort to available dispersion equations proposed for visible region by various investigators. From Table 6, the  $\epsilon_\infty$  values are 5.90 by Marple, 5.7032 by Wunderlich and DeShazer, and 5.925 by Feldman *et al.* It appears that the second value given above is somewhat too low in comparison with the others. However, recalling the narrow wavelength region coverage in the work of Wunderlich and DeShazer, the data over that wavelength region do not have enough dispersion to define the coefficients of a dispersion equation with certainty. Based on this consideration, a value approximately 5.91 has been taken as correct for  $\epsilon_\infty$ .

The values of  $\epsilon_0$  from Table 7 vary from 7.6 to 9.6. This variation also is far too large for refractive index calculations. None of the available dispersion equations indicates a more acceptable value except that reported by Hattori *et al.*<sup>19</sup> whose room-temperature measurements covered the spectral region between 165 to 540  $\mu\text{m}$ . By definition, the value of  $\epsilon_0$  equals the square of the refractive index measured at long wavelengths. The values from Hattori's work are 3.063 at 156  $\mu\text{m}$  and 2.999 at 540  $\mu\text{m}$ . An appropriate value of  $\epsilon_0$  is, therefore, approximately 9.0.

Among the values of  $\lambda_1$  from Table 7, those reported by Manabe *et al.*<sup>16</sup> are chosen. The value was determined by a transmission measurement on an evaporated thin film, a direct means for determining this property. The range of this value of  $\lambda_1$  is from 48.31 to 49.02  $\mu\text{m}$ .

The value of  $\lambda_u$  is very uncertain based on available dispersion equations: 0.325 and 0.336  $\mu\text{m}$  by Marple,<sup>48</sup> 0.26522  $\mu\text{m}$  by Wunderlich and DeShazer,<sup>53</sup> and 0.192 and 0.379  $\mu\text{m}$  or 0.201 and 0.392  $\mu\text{m}$  by Feldman *et al.*<sup>17</sup> Absorption peaks based on a reflectivity observation<sup>57</sup> are at 0.243, 0.261, 0.394, and 0.459  $\mu\text{m}$ . It appears, however, that the best value of  $\lambda_u$  should be around 0.3  $\mu\text{m}$ .

With all the essential parameters as discussed above at hand, the data of Feldman *et al.* are fitted to Eq. (9) for the determination of the constants  $A$  and  $B$  by allowing the parameters varying within their corresponding estimated limits. The dispersion equation of CVD ZnSe at room temperature thus obtained is

$$n^2 = 9.01536 + \frac{0.24482}{\lambda^2 - (0.29934)^2} + \frac{3.08889}{\lambda^2/48.38^2 - 1}, \quad (22)$$

where  $\lambda$  is in units of  $\mu\text{m}$ . This equation serves as a starting point to incorporate with the temperature-dependent data.

Equation (22) is valid in the wavelength range 0.55–18  $\mu\text{m}$ . In Fig. 13, deviations of the available room-temperature data from those calculated from Eq. (22) are plotted for visual comparison. It is clear that the data from various measurements are quite different from the values calculated from Eq. (22). While most of the data of Rambauske<sup>50</sup> are considerably lower than calculated values, those of Wunderlich and DeShazer<sup>53</sup> are higher in the corresponding spectral region. Such wide discrepancies arise from different material origins, and the data are very sensitive to impurity content of the sample, particularly in the short wavelength region. To show such sensitivity, a figure reported by Rambauske is reproduced in Fig. 14 where the two curves for two samples with different impurities disagree not only in absolute values but also in the shapes. This is particularly true in the wavelength region below 0.55  $\mu\text{m}$  where the impurity effects prevail and noting the energy gap of pure ZnSe is about 0.48  $\mu\text{m}$ . From Fig. 14, it appears that a purer sample should have a sharper dispersion curve. Based on this consideration, the sample used by Wunderlich and DeShazer contains less impurity than those used by Rambauske. In fact, the data of the former are in agreement with the values calculated from Eq. (22) in the region greater than 0.55  $\mu\text{m}$ , below which absorption becomes significant as it approaches the absorption edge and Eq. (22) becomes invalid.

Large discrepancies are also observed between the values from Eq. (22) and data of Marple.<sup>48</sup> As discussed earlier, these samples had a variety of impurities and the results from them differ by 0.005 in most of the wavelength region covered. This is not surprising because in comparison with other measurements, the samples appear similar to those of Rambauske as the data are similar in the region where measurements overlap.

Although Irtran 4 is considered a polycrystalline form of ZnSe, its refractive index is different from that of CVD ZnSe which is also polycrystalline in nature. As shown in Fig. 13, data from Eastman Kodak Publication U-72 (Ref. 21) are discrepant from Eq. (22) by an amount up to 0.0025 over the spectral range from 1 to 16  $\mu\text{m}$ , beyond which high-

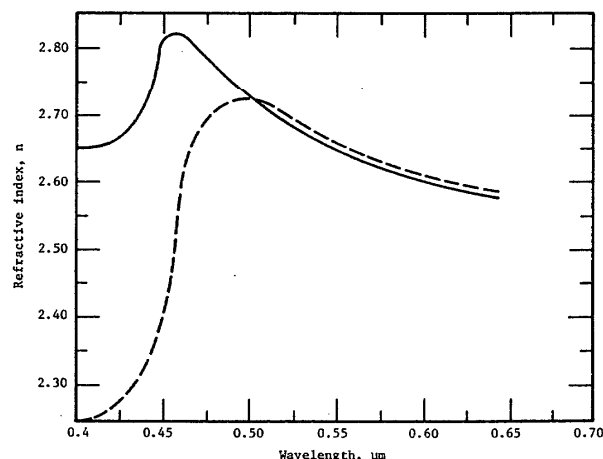


Figure 14. Dispersion curves for two different ZnSe samples reported in Ref. 50.

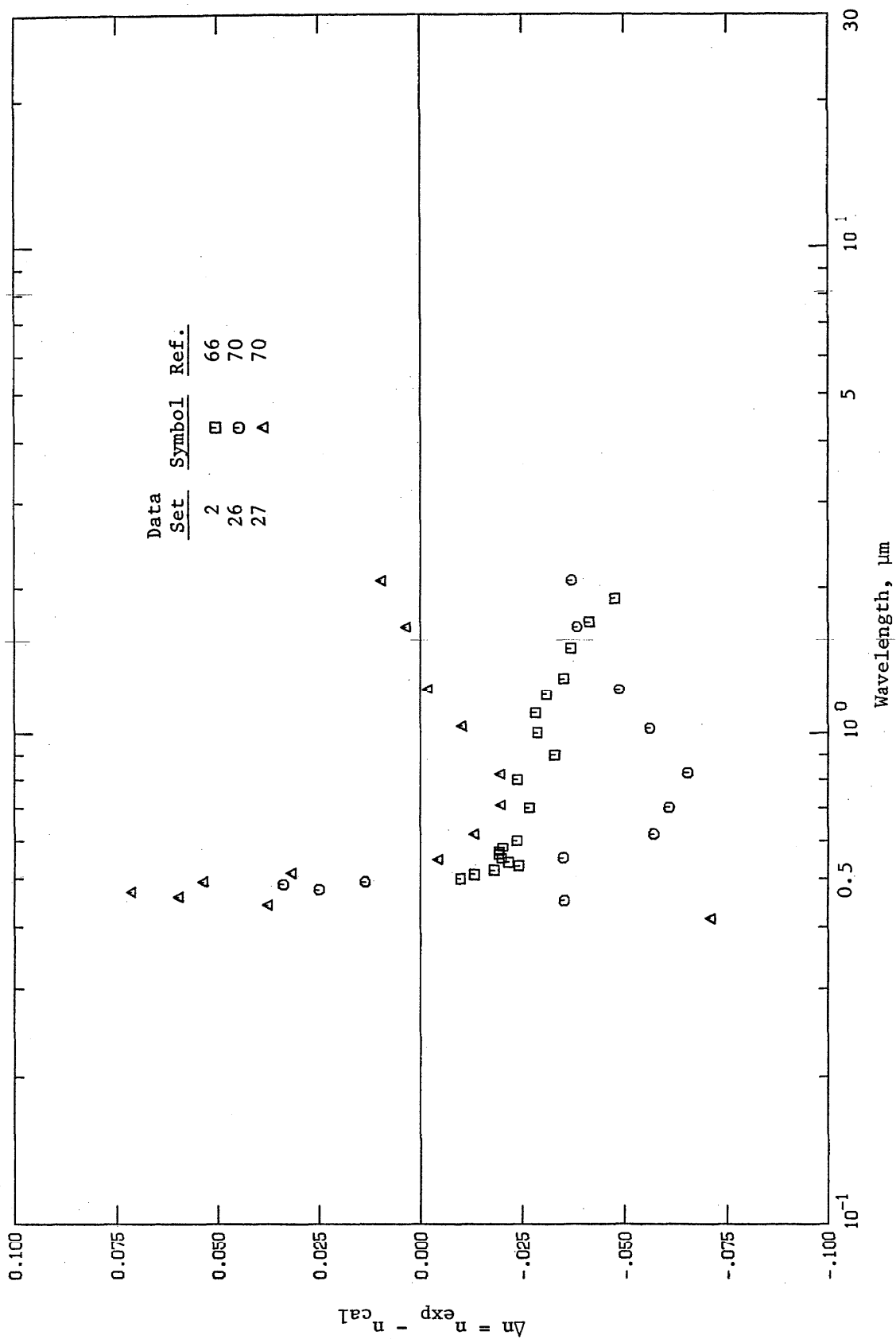


Figure 15. Comparison of experimental refractive indices of ZnSe films and calculated values for bulk ZnSe from Eq. (22). The calculated values are represented by the line  $\Delta n = 0$ .

er discrepancies are observed. Irtran 4 data reported by Hilton and Jones<sup>52</sup> seem to be scattered evenly around the calculated curve but these data may not be accurate as this data set was digitized from a graph. As discussed earlier in Sec. 3.1 for the case of ZnS, the refractive index of Irtran 2 is sample dependent and the same behavior is expected for Irtran 4.

Based on the considerations discussed above, it is concluded that Eq. (22) is valid for CVD ZnSe with uncertainty  $\pm 0.0004$  estimated from the average residual of least-squares data fitting and the highest disagreement between the two data sets of Feldman *et al.* Its validity for crystal ZnSe requires new data on high purity crystals.

In Fig. 15 are plotted the deviations of film ZnSe data from the calculated bulk data based on Eq. (22). Unlike ZnS where a definite trend of the deviation clearly exists, such behavior does not appear in Fig. 15. A possible reason is that we have only limited data sets<sup>66-68,70,71</sup> for statistical comparisons.

Equation (22) is also valid in the wavelength region 155–540  $\mu\text{m}$ . The averaged differences between the experimental data and the calculated values are in the order of  $\pm 0.003$ . The dispersion in this region is rather small as the difference of two extreme refractive indices is only 0.064 but the uncertainty in the data is rather large (of the order  $\pm 0.005$ ) as the data were digitized from a graph of low resolution. Under such condition, the reliability of the digitized values is compatible with the calculated ones.

### 3.2.3. Temperature-Dependent Dispersion Equation

Literature data on the temperature-dependent refractive index of ZnSe is extremely limited. Data plotted in Fig. 12 are measured by Thompson *et al.*<sup>54</sup> Additional data sets plotted in the same figure were derived from the  $dn/dT$  data reported by Feldman *et al.* (see Figs. 16 and 17).

Thompson *et al.*<sup>54</sup> reported refractive indices of two CVD ZnSe specimens at 3.8 and 10.6  $\mu\text{m}$  over the temperature range 80–300 K. Values for the two specimens, from different batches supplied by RCA Inc., were found to differ by a constant value of about 0.001 over the entire temperature range. This difference cannot be accounted for by the experimental error of  $\pm 0.0002$ . The possible cause might be attributed to differences in impurity content and crystal defects. Although the specimen data differ by an amount more than the experimental error, the temperature coefficients of refractive index in both cases are equal within the experimental error. Furthermore, the  $dn/dT$  values,  $7 \times 10^{-5} \text{K}^{-1}$  at 3.8  $\mu\text{m}$  and  $6 \times 10^{-5} \text{K}^{-1}$  at 10.6  $\mu\text{m}$ , show no evidence of temperature dependence in that temperature region. From Fig. 12, it is noticed that the data of Thompson *et al.* from 80 to 300 K differ uniformly from those of Feldman *et al.* by about 0.005 at 10.6  $\mu\text{m}$  and by about 0.002 at 3.8  $\mu\text{m}$ . These discrepancies are partly due to difference in materials and partly due to errors in digitizing from the graph given by Thompson *et al.* As a result, the Thompson data are not chosen in data analysis for large uncertainties in refractive index and for lack of dispersion in  $dn/dT$ .

Although Feldman *et al.* reported only room-temperature refractive index, their  $dn/dT$  data are reliable enough to

calculate the refractive index values at other temperatures from 93 to 473 K. The  $dn/dT$  data were measured by an interferometric technique at four discrete laser wavelengths: 0.6328, 1.15, 3.39, and 10.6  $\mu\text{m}$ . Equation (18) can be used for the determination of the constants  $E$ 's,  $A$ 's, and  $B$ 's. However, before a least-squares fit of data can be carried out, the following points have to be considered.

The temperature variation of  $\lambda_u$  and  $\lambda_l$  in Eqs. (13) and (18) can be defined using available literature data on the temperature shift of the energy gap and TO mode optical phonon. In a theoretical study of temperature derivative of refractive index in transparent crystals, Tsay *et al.*<sup>5</sup> calculated  $d\omega_g/dT$  based on a pseudopotential method. In terms of wavelength shift, their result for ZnSe is  $d\lambda_g/dT = 1.004 \times 10^{-4} \mu\text{m K}^{-1}$ . Based on the fact that the  $d\lambda_g/dT$  of ZnS remains a constant over a wide temperature range,<sup>1</sup> the same is assumed to be true for ZnSe. This value is adopted for the parameter  $\lambda_u$  in Eq. (13) in view of that  $\lambda_u$ , although not exactly corresponding to energy gap, is the effective absorption band and that the quoted shift is small enough not to introduce much effect on the refractive index as a whole. We have, therefore,

$$\lambda_u = \lambda_{u0} + \beta_u t = 0.29934 + 1.004 \times 10^{-4} t,$$

where  $\lambda_{u0}$  is determined at room temperature as indicated in Eq. (22). The experimental value for the temperature shift of  $\lambda_l$  of ZnSe was found to be  $1/\lambda_l d\lambda_l/dT = 1.3 \times 10^{-4} \text{K}^{-1}$  by LaCombe and Irwing.<sup>6</sup> Using  $\lambda_{l0} = 48.38$ , the corresponding value of  $\beta_l$  is  $0.00629 \mu\text{m K}^{-1}$  and  $\lambda_l = 48.38 + 0.00629t$ .

A careful study of Fig. 16 shows large discrepancies occurring at the wavelength 10.6  $\mu\text{m}$  where a number of measurements using the CO<sub>2</sub> laser are available. The large disagreement is best shown by the work of Skolnik and Clark<sup>63</sup> who measured  $dn/dT$  for two types of samples, the Irtran 4 and Raytheon CVD ZnSe. They found that the  $dn/dT$  value of the latter sample is twice that of the former though both samples have essentially the same density. Since the  $dn/dT$  of Irtran 4 is in agreement with that of other investigators who reported data for CVD ZnSe, the Raytheon sample must be very different from the other CVD ZnSe samples. Unfortunately, the origin of such a large discrepancy is not understood at present.

A careful examination of Fig. 17 clearly shows that for all four data sets,  $dn/dT$  increases with  $T$  in the region between 93 K and room temperature and remains practically constant thereafter up to 400 K. Above 400 K,  $dn/dT$  appears to increase with increasing temperature, an observation supported by the work of Mangir and Hellwart.<sup>64</sup> They observed that within the experimental uncertainty,  $0.2 \times 10^{-5} \text{K}^{-1}$ , there is no variation of  $\Delta n/\Delta T$  values over the temperature range from 293 to 473 K, but at higher temperatures up to 600 K, a small constant increase at a rate of  $0.5 \times 10^{-5}$  per 100 K was observed at all wavelengths. Their measurements stopped at 600 K.

With all these considerations, a least-squares fit of  $dn/dT$  data to Eq. (18) yielded the following expression for the refractive index of ZnSe as a function of both wavelength

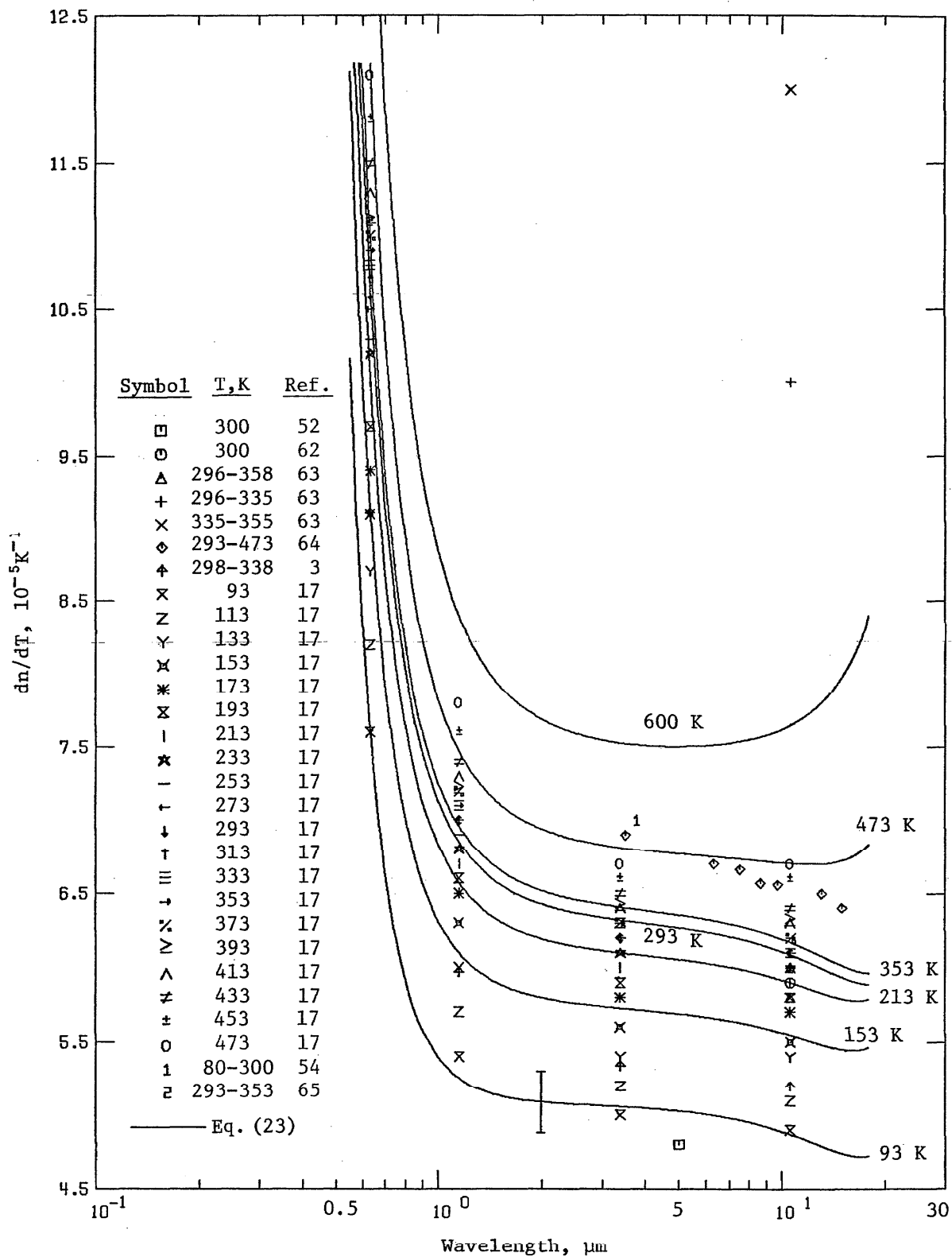


Figure 16. Experimental and calculated  $dn/dT$  of ZnSe (wavelength dependence).

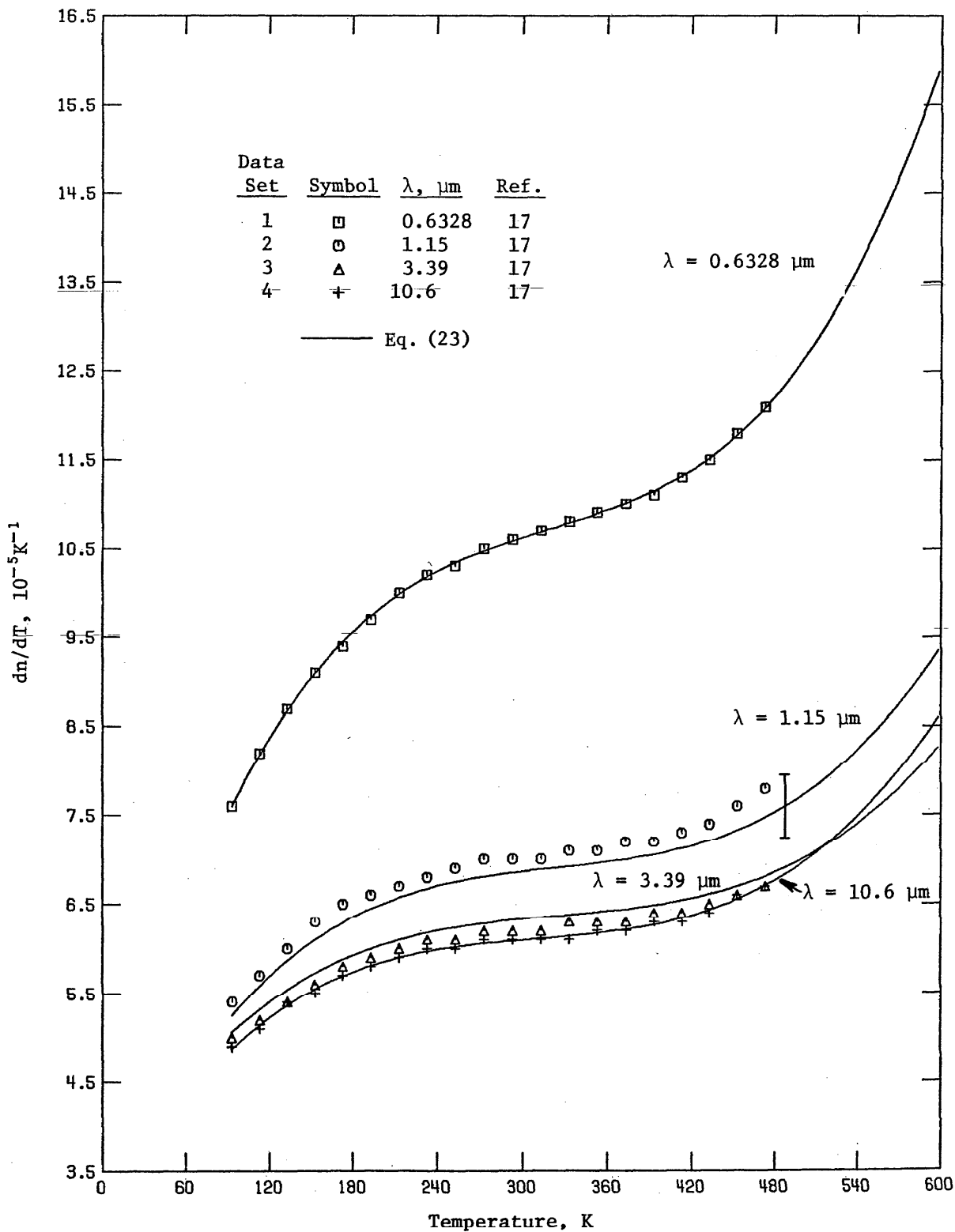


Figure 17. Experimental and calculated  $dn/dT$  of ZnSe (temperature dependence).





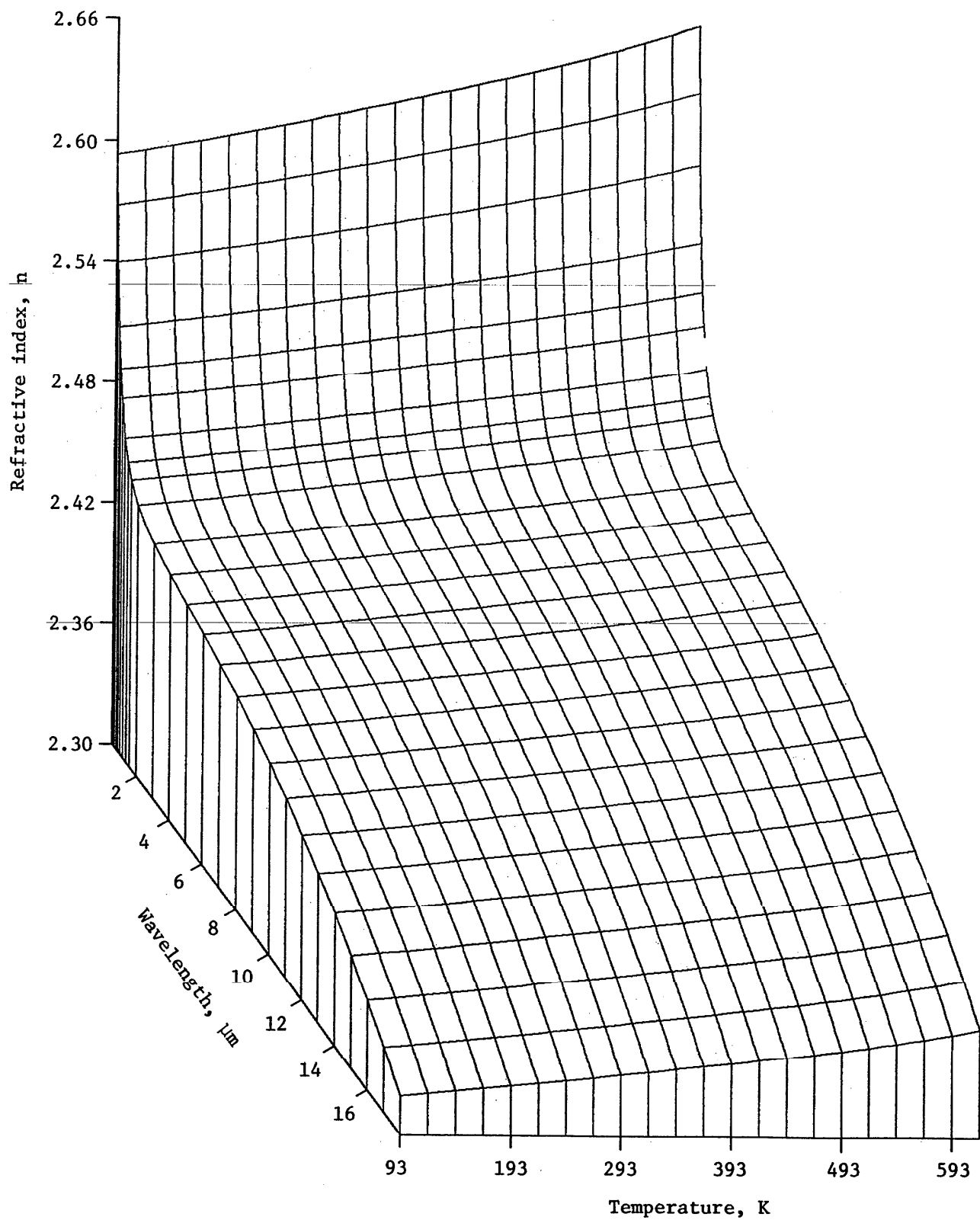


Figure 18. Recommended  $n$ - $\lambda$ - $T$  diagram of ZnSe.

Table 9. Recommended values (in units of  $10^{-5}\text{K}^{-1}$ ) on the temperature derivative of refractive index of CVD ZnSe

$\lambda$ , $\mu\text{m}$	Temperature, K											
	93	143	193	243	293	343	393	443	493	543	593	618
0.55	10.2	11.9	13.0	13.8	14.3	14.8	15.3	16.2	17.4	19.3	21.9	23.6
0.60	8.4	9.8	10.7	11.3	11.7	12.0	12.4	13.0	13.9	15.4	17.5	18.8
0.65	7.3	8.5	9.3	9.8	10.1	10.4	10.6	11.1	11.9	13.1	14.9	16.0
0.70	6.6	7.8	8.5	8.9	9.2	9.3	9.6	10.0	10.6	11.7	13.3	14.3
0.75	6.2	7.2	7.9	8.3	8.5	8.7	8.8	9.2	9.8	10.7	12.1	13.1
0.80	5.9	6.9	7.5	7.8	8.0	8.2	8.3	8.7	9.2	10.1	11.4	12.2
0.85	5.7	6.6	7.2	7.5	7.7	7.8	8.0	8.3	8.8	9.6	10.8	11.6
0.90	5.6	6.4	7.0	7.3	7.5	7.6	7.7	8.0	8.5	9.2	10.4	11.1
0.95	5.5	6.3	6.8	7.1	7.3	7.4	7.5	7.8	8.2	8.9	10.0	10.7
1.0	5.4	6.2	6.7	7.0	7.1	7.2	7.4	7.6	8.0	8.7	9.8	10.4
1.5	5.1	5.8	6.2	6.4	6.6	6.6	6.7	6.9	7.3	7.8	8.7	9.2
2.0	5.1	5.7	6.1	6.3	6.4	6.5	6.6	6.8	7.1	7.6	8.4	8.9
2.5	5.1	5.7	6.0	6.3	6.4	6.4	6.5	6.7	7.0	7.5	8.2	8.7
3.0	5.1	5.6	6.0	6.2	6.3	6.4	6.5	6.7	7.0	7.5	8.2	8.7
3.5	5.1	5.6	6.0	6.2	6.3	6.4	6.5	6.6	6.9	7.4	8.2	8.6
4.0	5.0	5.6	6.0	6.2	6.3	6.4	6.5	6.6	6.9	7.4	8.2	8.6
4.5	5.0	5.6	6.0	6.2	6.3	6.4	6.4	6.6	6.9	7.4	8.2	8.6
5.0	5.0	5.6	6.0	6.2	6.3	6.3	6.4	6.6	6.9	7.4	8.2	8.6
5.5	5.0	5.6	5.9	6.1	6.3	6.3	6.4	6.6	6.9	7.4	8.2	8.7
6.0	5.0	5.6	5.9	6.1	6.2	6.3	6.4	6.6	6.9	7.4	8.2	8.7
6.5	5.0	5.6	5.9	6.1	6.2	6.3	6.4	6.6	6.9	7.4	8.2	8.7
7.0	5.0	5.6	5.9	6.1	6.2	6.3	6.4	6.6	6.9	7.4	8.2	8.7
7.5	5.0	5.5	5.9	6.1	6.2	6.3	6.4	6.6	6.9	7.4	8.3	8.8
8.0	5.0	5.5	5.9	6.1	6.2	6.2	6.3	6.5	6.9	7.5	8.3	8.8
8.5	4.9	5.5	5.9	6.1	6.2	6.2	6.3	6.5	6.9	7.5	8.3	8.9
9.0	4.9	5.5	5.9	6.0	6.1	6.2	6.3	6.5	6.9	7.5	8.3	8.9
9.5	4.9	5.5	5.8	6.0	6.1	6.2	6.3	6.5	6.9	7.5	8.4	9.0
10.0	4.9	5.5	5.8	6.0	6.1	6.2	6.3	6.5	6.9	7.5	8.4	9.0
10.5	4.9	5.5	5.8	6.0	6.1	6.2	6.3	6.5	6.9	7.5	8.5	9.1
11.0	4.9	5.4	5.8	6.0	6.1	6.1	6.3	6.5	6.9	7.6	8.5	9.1
11.5	4.8	5.4	5.8	6.0	6.1	6.1	6.2	6.5	6.9	7.6	8.6	9.2
12.0	4.8	5.4	5.8	6.0	6.1	6.2	6.2	6.5	6.9	7.6	8.6	9.3
12.5	4.8	5.4	5.8	5.9	6.0	6.1	6.2	6.5	6.9	7.6	8.7	9.4
13.0	4.8	5.4	5.7	5.9	6.0	6.1	6.2	6.4	6.9	7.7	8.7	9.5
13.5	4.8	5.4	5.7	5.9	6.0	6.0	6.2	6.4	6.9	7.7	8.8	9.5
14.0	4.8	5.4	5.7	5.9	6.0	6.0	6.2	6.4	6.9	7.7	8.9	9.6
14.5	4.8	5.4	5.7	5.9	6.0	6.0	6.1	6.4	7.0	7.8	9.0	9.7
15.0	4.7	5.4	5.7	5.9	5.9	6.0	6.1	6.4	7.0	7.8	9.1	9.9
15.5	4.7	5.4	5.7	5.9	5.9	6.0	6.1	6.4	7.0	7.9	9.2	10.0
16.0	4.7	5.4	5.7	5.9	5.9	6.0	6.1	6.4	7.0	7.9	9.3	10.1
16.5	4.7	5.4	5.7	5.8	5.9	6.0	6.1	6.4	7.0	8.0	9.4	10.3
17.0	4.7	5.4	5.7	5.8	5.9	5.9	6.1	6.4	7.1	8.1	9.5	10.4
17.5	4.7	5.4	5.7	5.8	5.9	5.9	6.1	6.5	7.1	8.1	9.6	10.6
18.0	4.7	5.4	5.7	5.8	5.9	5.9	6.1	6.5	7.1	8.2	9.8	10.7

Uncertainties in the recommended  $dn/dT$  values are estimated based on the results of data fitting calculation and those reported by Feldman *et al.* which are the primary data source for Eq. (23). Their reported uncertainties are

$\pm 0.1 \times 10^{-5}\text{K}^{-1}$  at all the four wavelengths investigated. Our calculations, however, indicated a higher value of  $\pm 0.2 \times 10^{-5}\text{K}^{-1}$ . Error bars corresponding to the latter are indicated in Figs. 16 and 17 where calculations are compared with experimental data. Uncertainties of the recommended  $dn/d\lambda$  values can be estimated based on Eq. (21) using  $\delta n = \pm 0.0004$ .

Table 10. Recommended values on the wavelength derivative of refractive index of CVD ZnSe

$\lambda$ , $\mu\text{m}$	$-\frac{dn}{d\lambda}$ , $10^{-3}\mu\text{m}^{-1}$	$\lambda$ , $\mu\text{m}$	$-\frac{dn}{d\lambda}$ , $10^{-3}\mu\text{m}^{-1}$
0.55	1117.1 <sup>a</sup>	7.5	4.5
0.60	769.0	8.0	4.8
0.65	556.7	8.5	5.1
0.70	418.5	9.0	5.4
0.75	323.9	9.5	5.7
0.80	256.6	10.0	6.1
0.85	207.2	10.5	6.4
0.90	170.1	11.0	6.8
0.95	141.6	11.5	7.2
1.0	119.2	12.0	7.6
1.5	32.8	12.5	8.0
2.0	14.2	13.0	8.4
2.5	8.0	13.5	8.8
3.0	5.4	14.0	9.3
3.5	4.3	14.5	9.8
4.0	3.8	15.0	10.3
4.5	3.6	15.5	10.8
4.8 <sup>b</sup>	3.58 <sup>b</sup>	16.0	11.3
5.0	3.6	16.5	11.9
5.5	3.7	17.0	12.5
6.0	3.8	17.5	13.1
6.5	4.0	18.0	13.7
7.0	4.3		

<sup>a</sup>The uncertainties of  $dn/d\lambda$  (in units of  $10^{-3}\mu\text{m}^{-1}$ ) are:  $\pm 4$  at 0.6  $\mu\text{m}$ ,  $\pm 2$  at 1  $\mu\text{m}$ ,  $\pm 0.3$  at 5  $\mu\text{m}$ ,  $\pm 0.2$  at 10  $\mu\text{m}$ ,  $\pm 0.1$  at 15  $\mu\text{m}$ , and  $\pm 0.1$  at 18  $\mu\text{m}$ .

<sup>b</sup>Minimum point on the curve.

### 3.3. Zinc Telluride, ZnTe

There are 22 sets of experimental data available for the refractive index of zinc telluride as plotted in Fig. 21 where some of the data sets for thin films are included. It should be noted that all of these available data are at room temperature except those of Hattori *et al.*<sup>19</sup> Presently, refractive index data in the fundamental transparent region at other temperatures are not yet available and as a result, our data analysis is limited to room temperature. The refractive index of bulk ZnTe in the transparent region is reported by Aten *et al.*,<sup>72</sup> Shiozawa *et al.*,<sup>73-75,78,79</sup> Marple,<sup>48</sup> and Horikoshi.<sup>80</sup> Data sets reported by Hattori *et al.* are the only available data in the far infrared wavelength range, from about 102 to 583  $\mu\text{m}$ . Data reported by Manabe *et al.*<sup>16</sup> and by Hadni *et*

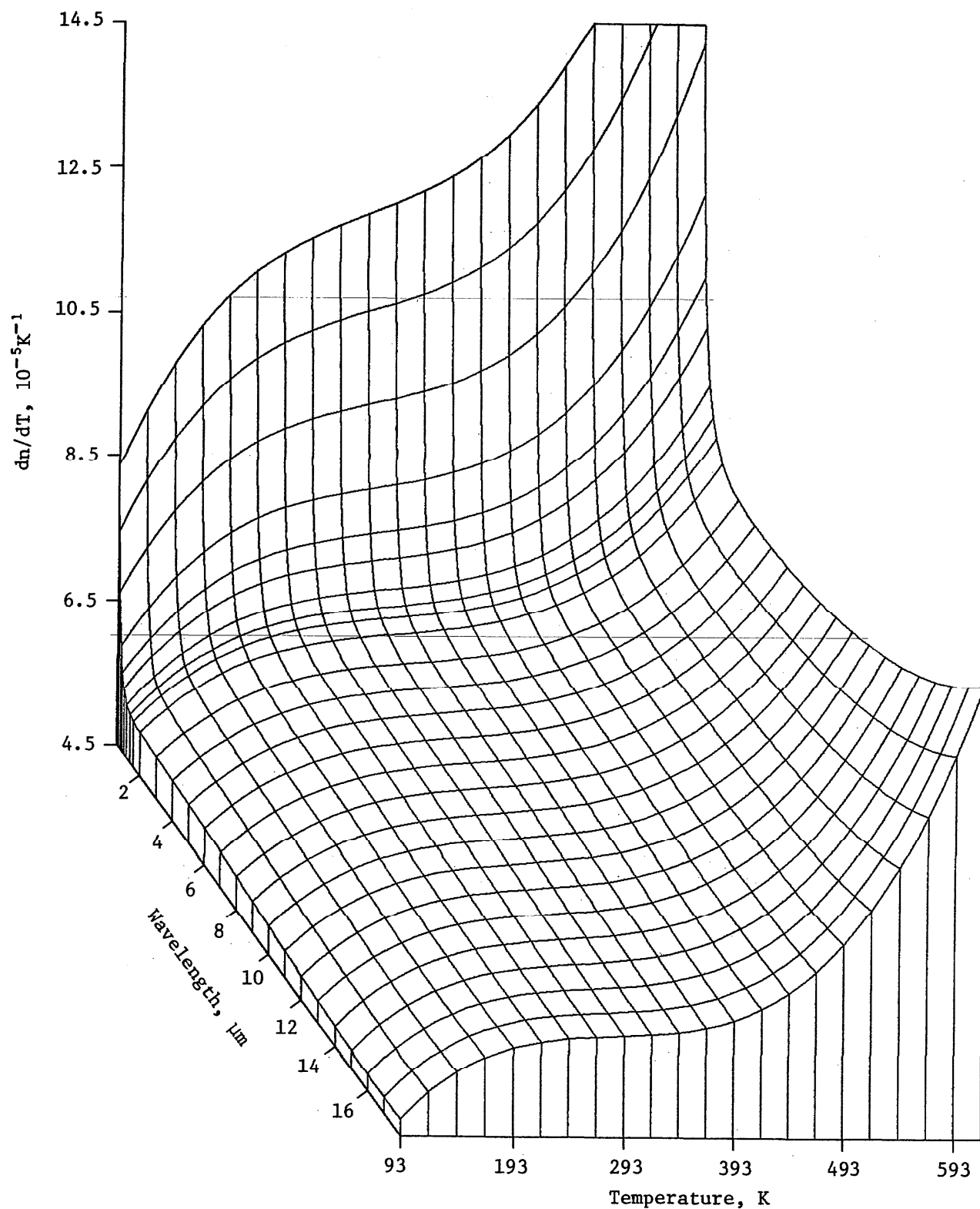


Figure 19. Recommended  $dn/dT$ - $\lambda$ - $T$  diagram of ZnSe.

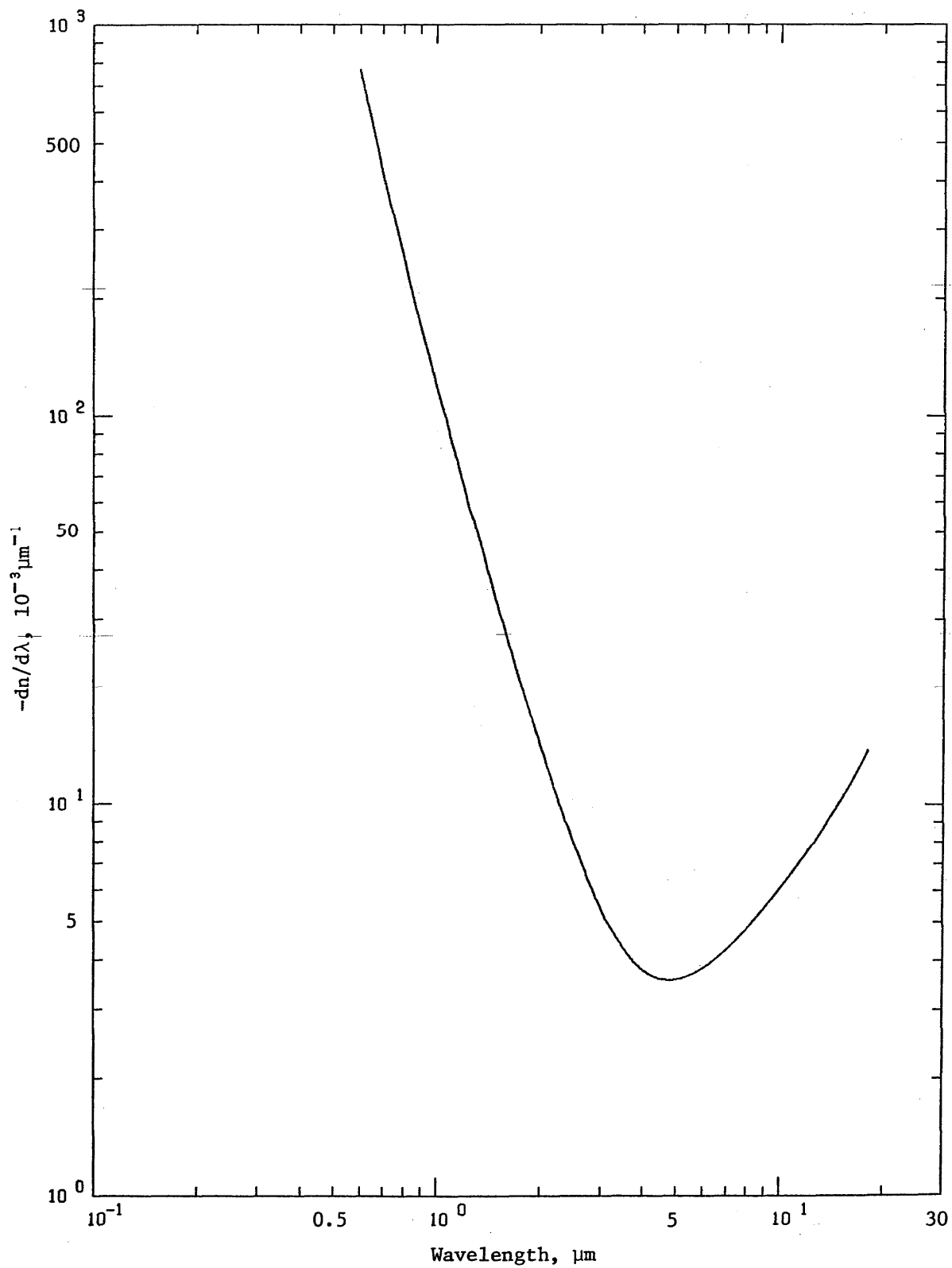


Figure 20. Recommended  $dn/d\lambda$  curve of ZnSe at 293 K.

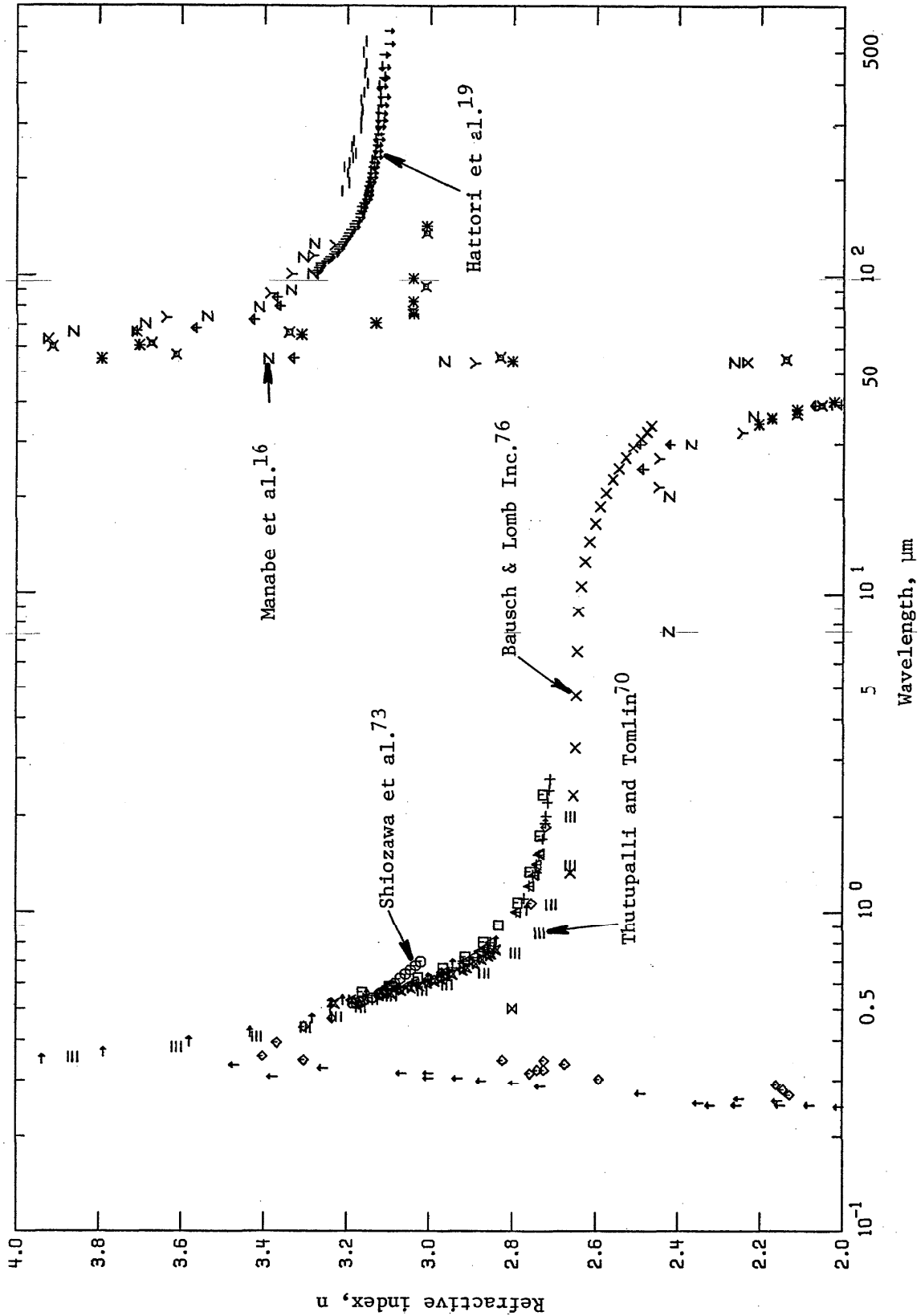


Figure 21. Available experimental refractive index of ZnTe (wavelength dependence).

*al.*<sup>55,56</sup> cover characteristics of the reststrahlen region. The data of Cardona<sup>77</sup> are in the electronic absorption region.

### 3.3.1. Review of Available Data

In an effort to study the direct and phonon-assisted optical transitions in zinc telluride, Aten *et al.* measured the refractive index over a wavelength range from 0.56 to 2.34  $\mu\text{m}$  to determine the parameters correlating the energies of longitudinal and transverse phonons. Although the refractive index data were obtained with the minimum deviation method for a sample of very low impurity concentration, the data are expected to have uncertainties in the second decimal place for they were digitized from a graph of low resolution.

Shiozawa *et al.* reported two sets of data for synthetic crystals of ZnTe measured with the minimum deviation method. The first data set was observed over the visible region for a small sample with apparent impurities. The results were considered as preliminary and were plotted in the form of  $1/(n^2 - 1)$  versus  $1/\lambda^2$  in order to test the form of the dispersion. The measured values were linear, but the predicted value for optical dielectric constant of 8.24 is much higher than that of purer samples. The second set was obtained over an extended wavelength range from 0.569 to 1.515  $\mu\text{m}$  for a purer crystal containing some twinning and cut from a boule grown by sublimation method. The reported uncertainty of the refractive index measurements is  $\pm 0.002$ . The optical dielectric constant predicted by this data set is  $7.26 \pm 0.03$ , in agreement with the accepted values.

For the purpose of obtaining consistent refractive indices of ZnTe over a wavelength range from the short-wave transmission limit to 2.06  $\mu\text{m}$ , Marple<sup>48,49</sup> measured the refractive index of two samples grown by sublimation in an argon atmosphere. The amount of impurity was 10–20 ppm. The reported experimental error is  $\pm 0.003$  or less; the results for two prisms differ by up to 0.003 in the entire wavelength region consistently, which is within the possible combined experimental error of the two sets of data. As shown in Table 11, the equation  $n^2 = A + B\lambda^2/(\lambda^2 - C^2)$  was used to fit experimental data for each prism with  $A$ ,  $B$ , and  $C$  being adjustable parameters. The best-fit values of  $A$ ,  $B$ , and  $C$  for each of the two prisms indicate an average value of 7.28 for the optical dielectric constant of ZnTe.

Similar to Marple's work, Horikoshi *et al.*<sup>80</sup> measured the refractive index of ZnTe samples containing detectable impurities of the order of 100 ppm. The crystals were grown by a vapor phase technique in a vacuum, in an argon atmosphere, or from a melt. The average refractive indices from this method were again fitted to an equation of the form of  $n^2 = A + B\lambda^2/(\lambda^2 - C^2)$  as given in Table 11. Although the experimental error was not reported with the data, it is likely to be of the order  $\pm 0.01$ , as estimated from their graphical presentation. As compared with the data of other investigators, their samples yield results (see Table 11) closely agreeing to those measured by Marple for the constants  $A$ ,  $B$ , and  $C$  in the dispersion equations. For ease of comparison, the differences between the above mentioned data sets and the recommended values for the transparent region are plotted in Fig. 22.

The indices of refraction of ZnTe in the far infrared

spectral range from 102 to 584  $\mu\text{m}$  were measured by Hattori *et al.*<sup>19</sup> at temperatures 2, 80, and 300 K. The results were described by a simple dispersion equation from which the static dielectric constant, optical dielectric constant, and wavelength of TO mode phonon were determined. The static dielectric constant serves as a check for the  $\epsilon_0$  values reported by the other investigators. Since the data were measured by an interference method over long wavelength region, the value of  $\epsilon_0$  is believed to be reliable and should be adopted as a known parameter in the dispersion equation of ZnTe.

Manabe *et al.*<sup>16</sup> studied optical constants in the reststrahlen region by means of the infrared lattice reflection spectra in the spectral region between 20 and 85  $\mu\text{m}$  using the Drude dispersion relation. The oscillator strength  $N$ , optical dielectric constant  $\epsilon_\infty$ , damping factor  $\delta$ , and wavelength of transverse optical phonon  $\lambda_1$ , in the Drude equations (shown in Tables 11 and 12) were determined by least-squares fit of reflectivity data. The wavelength of transverse optical phonon was also determined directly from a transmission spectrum of an evaporated thin film and was found to agree with that obtained from the reflection spectra analysis. The static dielectric constant  $\epsilon_0$  was determined by letting  $\lambda = \infty$  in the resulting Drude equation assuming zero absorption. Optical constants in the reststrahlen region were also studied by Hadni *et al.*<sup>55,56</sup> for a ZnTe pellet sample at temperatures 80 and 290 K. The various parameters  $\epsilon_0$ ,  $\epsilon_\infty$ , and  $\lambda_1$ , were determined from the reflection and transmission spectra using the Kramers–Kronig relations and the Lorentz one-oscillator model as shown in Table 11. Cardona<sup>77</sup> investigated the optical properties in the ultraviolet region determining the optical dielectric constant using Penn's model based on the peak positions in the ultraviolet spectra. The value of  $\epsilon_\infty$  (7.2) determined from reflectivity peaks agree well with those from dispersion equations of other investigators.

### 3.3.2. Room-Temperature Dispersion Equation

From the brief review of the available data given above, it is clear that the correct values of the parameters  $\epsilon_0$ ,  $\epsilon_\infty$ , and  $\lambda_1$  for Eq. (9) are about 9.92, 7.26, and 56.5  $\mu\text{m}$ , respectively. The choice of reliable data for the determination of the constants  $A$ ,  $B$ , and  $\lambda_0$  is discussed below. It was noted in the case of ZnSe that the data sets reported by Marple differ significantly from the other measurements and lack internal consistency between different samples because of impurity contents. Although the ZnTe samples measured by him have impurity levels as high as in his ZnSe samples, it is found that the refractive index of ZnTe is not so sensitive to the impurity contents as in the case of ZnSe samples. First, the two data sets reported by Marple for different samples agree within the experimental error. Second, the data by Shiozawa *et al.*, though for samples having crystal defects of different nature, agree with the data by Marple within the errors combined, i.e.,  $\pm 0.005$ . Additional evidence is that the sample used by Horikoshi *et al.*<sup>80</sup> has impurities five times higher than that used by Marple, yet their data agree within the experimental uncertainties. Based on these considerations and the wide spectral coverage, the data set by Marple was taken as the basis for the data fitting calculation.

Table 11. Comparison of dispersion equations proposed for ZnTe

Source	Wavelength and temperature ranges	Dispersion equation $\lambda$ in $\mu\text{m}$ , $\Omega = \lambda_I/\lambda$
Marple, D.T.F., 1964; Ref. 48	0.57-2.6 $\mu\text{m}$ 298 K	for one sample: $n^2 = 3.96 + \frac{3.29 \lambda^2}{\lambda^2 - (0.366)^2}$ for less pure sample: $n^2 = 4.58 + \frac{2.72 \lambda^2}{\lambda^2 - (0.3875)^2}$
Manabe, A., Mitsuishi, A., Yoshinaga, H., 1967; Ref. 16	24-85 $\mu\text{m}$ at 300 K 42-67 $\mu\text{m}$ at 100 K	$n^2 - k^2 = \epsilon_\infty + \frac{N(1-\Omega^2)}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ $2nk = \frac{N\delta\Omega}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ at 300 K: $\epsilon_\infty = 6.7$ , $\lambda_I = 56.50 \mu\text{m}$ , $\delta = 0.017$ , and $N = 2.4$ ; at 100 K: $\epsilon_\infty = 6.7$ , $\lambda_I = 55.56 \mu\text{m}$ , $\delta = 0.013$ , and $N = 2.4$ .
Handi, A., Henry, P., Lambert, J.P., Morlot, G., Strimer, P., and Chanal, D., 1967; Ref. 55	36-136 $\mu\text{m}$ at 290 K 34-144 $\mu\text{m}$ at 80 K	$n^2 - k^2 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)(1-\Omega^2)}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ $2nk = \frac{(\epsilon_0 - \epsilon_\infty)\delta\Omega}{(1-\Omega^2)^2 + \delta^2\Omega^2}$ at 290 K: $\epsilon_\infty = 6.2$ , $\epsilon_0 = 8.3$ , $\lambda_I = 56.5 \mu\text{m}$ , and $\delta = 0.075$ ;
Handi, A., et al., 1967; Ref. 55 cont.		at 90 K: $\epsilon_\infty = 6.1$ , $\epsilon_0 = 8.3$ , $\lambda_I = 55.34 \mu\text{m}$ , and $\delta = 0.063$ .
Hattori, T., Homma, Y., Mitsuishi, A., and Tacke, M., 1973; Ref. 19	184-542 $\mu\text{m}$ at 300 K 161-452 $\mu\text{m}$ at 80 K 102-584 $\mu\text{m}$ at 2 K	$n^2 = \frac{\epsilon_0 - \epsilon_\infty\Omega^2}{1 - \Omega^2}$ at 300 K: $\epsilon_0 = 9.92$ , $\epsilon_\infty = 6.0$ , and $\lambda_I = 55.56 \mu\text{m}$ ; at 80 K: $\epsilon_0 = 9.65$ , $\epsilon_\infty = 6.2$ , and $\lambda_I = 52.63 \mu\text{m}$ ; at 2 K: $\epsilon_0 = 9.63$ , $\epsilon_\infty = 6.3$ , and $\lambda_I = 52.08 \mu\text{m}$ .
Horikoshi, Y., Ebina, A., and Takahashi, T., 1972; Ref. 80	0.55-0.76 $\mu\text{m}$ at 300 K 97 K	at 300 K: $n^2 = 4.56 + \frac{2.7090 \lambda^2}{\lambda^2 - (0.38637)^2}$ at 97 K: $n^2 = 4.36 + \frac{2.4615 \lambda^2}{\lambda^2 - (0.38451)^2}$
Present work, 1982	0.55-30 $\mu\text{m}$ at 293 K	$n^2 = 9.92 + \frac{0.42530}{\lambda^2 - (0.37766)^2}$ $+ \frac{2.63580}{\lambda^2/56.5^2 - 1}$



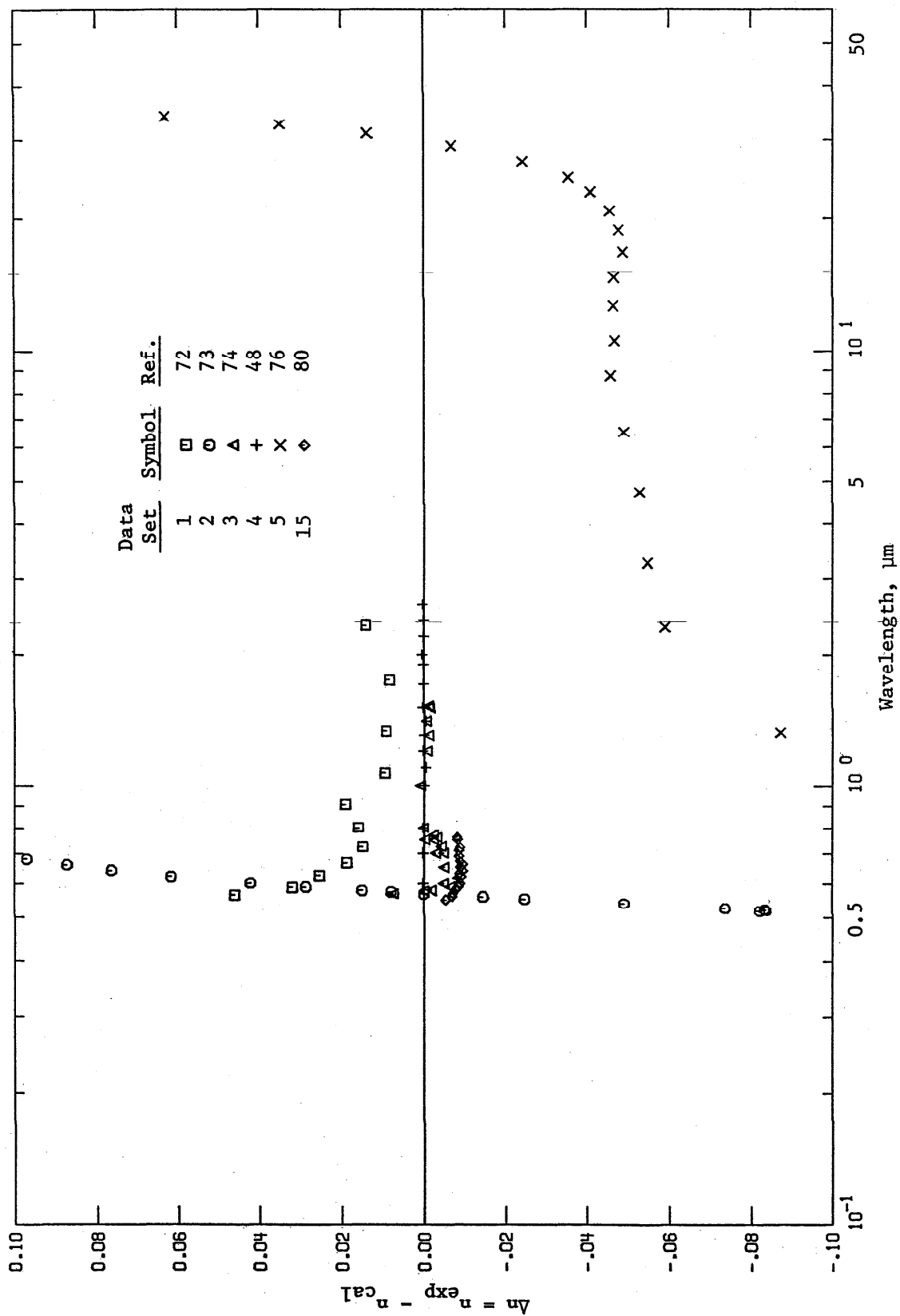


Figure 22. Comparison of experimental and calculate, refractive index values of ZnTe at room temperature. The calculated values from Eq. (24) are represented by the line  $\Delta n = 0$ .

Table 12. Available data on  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $\lambda_I$  of ZnTe

Temp., K	$\epsilon_\infty$	$\epsilon_0$	$\lambda_I$ , $\mu\text{m}$	Ref.
300	6.7	9.1	56.50, 55.87	16
300		10.10		24
300	7.28			48
300			56.34	82
300	6.0	9.92	55.56	19
300	6.2	8.3	56.50	56
300	6.7	9.1	56.50	59
300			52.63	27
300			56.50	61
300	7.26			79
300		18.6		83
300		10.1		7
80	6.2	9.65	52.63	19
80	6.1	8.3	55.34	56
80	6.7	9.1	55.56	59
80	6.7	9.1	55.56	16
2	6.3	9.63	52.08	19

The selected data set is numerically fitted to Eq. (9). Since the available data is limited to the region between 0.57 and 2.6  $\mu\text{m}$  while the transparent region of ZnTe extends up to 30  $\mu\text{m}$ , it is necessary to hold the parameters  $\epsilon_0$  and  $\lambda_I$  at fixed values, 9.92 and 56.5  $\mu\text{m}$ . This was done with some confidence because in the cases of ZnS and ZnSe, the best-fit values of  $\epsilon_0$  and  $\lambda_I$  was found to agree closely with the selected values. It is reasonable to assume that uncertainties in refractive index of ZnTe can be held at minimum as long as the parameter values come from the same sources. The dispersion equation for ZnTe at room temperature thus obtained is

$$n^2 = 9.92 + \frac{0.42530}{\lambda^2 - (0.37766)^2} + \frac{2.63580}{\lambda^2/56.5^2 - 1}, \quad (24)$$

where  $\lambda$  is in units of  $\mu\text{m}$ . Equation (24) is valid in the wavelength range from 0.57 to 30  $\mu\text{m}$ . In Fig. 22, deviations of available data in the fundamental transparent region from those calculated from Eq. (24) are plotted for comparison; a data set for film from Bausch and Lomb Inc.<sup>76</sup> is also included. It is interesting to note that the dispersion data from Bausch and Lomb is consistent with Eq. (24) in the spectral range from 2 to 20  $\mu\text{m}$ ; however, a large difference is observed at 1  $\mu\text{m}$  and beyond 20  $\mu\text{m}$ . A careful examination of the data from Ref. 76 shows the reported data at wavelengths greater than 20  $\mu\text{m}$  are questionable. To make the point more clearly, the data from Ref. 76 is reproduced in Fig. 23. If the deviant data point at the upper right of the figure was not included, the curve in the wavelength region greater than 20  $\mu\text{m}$  would be considerably lowered and dispersion in that region would likely be consistent with that of Eq. (24). This data point was either measured with very large

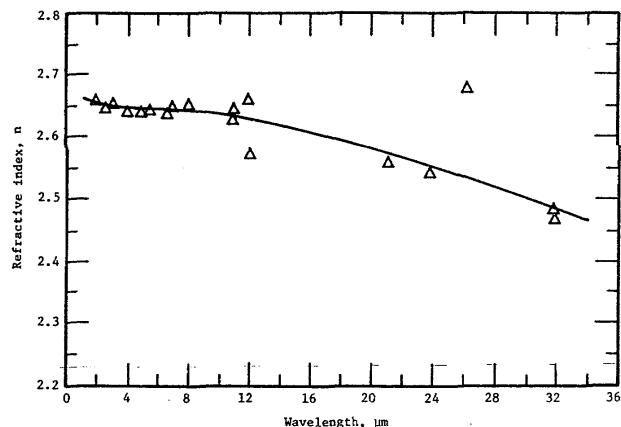


Figure 23. Measured dispersion of a ZnTe film reported in Ref. 76.

uncertainty or was affected by an unknown mechanism. At any rate, the departure from consistent dispersion behavior shown in Fig. 23 is simply attributed to the decision made by the investigators on the shape of the curve. Other data sets for films shown in Fig. 24 seem to support the idea that film has normal dispersion as its corresponding bulk material.

Equation (24) has been used to calculate the recommended values of the refractive index and  $dn/d\lambda$  of ZnTe at room temperature. The recommended values are given in Table 13 and plotted in Figs. 25 and 26 together with the experimental data sets discussed before. Uncertainties in the calculated values are estimated as follows. In the wavelength region between 0.57 to 2.6  $\mu\text{m}$ , the estimated uncertainties are  $\pm 0.003$  based on the uncertainties reported by Marple. In the region between 2.6 and 15  $\mu\text{m}$ , larger uncertainties of the order  $\pm 0.005$  are estimated because there is no experimental data available at wavelengths greater than 2.6  $\mu\text{m}$ . Since the dispersion in this region is low, uncertainties should not be very much different from Marple's data. In the region between 15 and 30  $\mu\text{m}$ , larger uncertainties are expected as the dispersion increases with wavelength approaching the reststrahlen region. The estimated upper limit of uncertainties in this region can be calculated from the expression

$$\pm \Delta n = 0.005 + \frac{B\lambda^2 \Delta\lambda_I}{2n\lambda_I^3(\lambda^2/\lambda_I^2 - 1)^2}, \quad (25)$$

where  $\Delta\lambda_I = 0.63$  corresponds to the difference of the two possible  $\lambda_I$  values reported by Manabe<sup>16</sup> (see Table 12).

Equation (24) is also valid in the wavelength region 184–541  $\mu\text{m}$ . The averaged differences between the experimental data and the calculated values are of the order of  $\pm 0.009$ . The dispersion in this region is rather small as the difference of two extreme refractive indices is only 0.059 but the uncertainty in the data is rather large (of the order  $\pm 0.005$ ) as the data were digitized from a graph of low resolution. Under such condition, the reliability of the digitized values is compatible with the calculated ones. Therefore, no recommended values in this region are given.

Uncertainties of the recommended  $dn/d\lambda$  values are estimated based on Eq. (21) using  $\delta n = \pm 0.005$ .

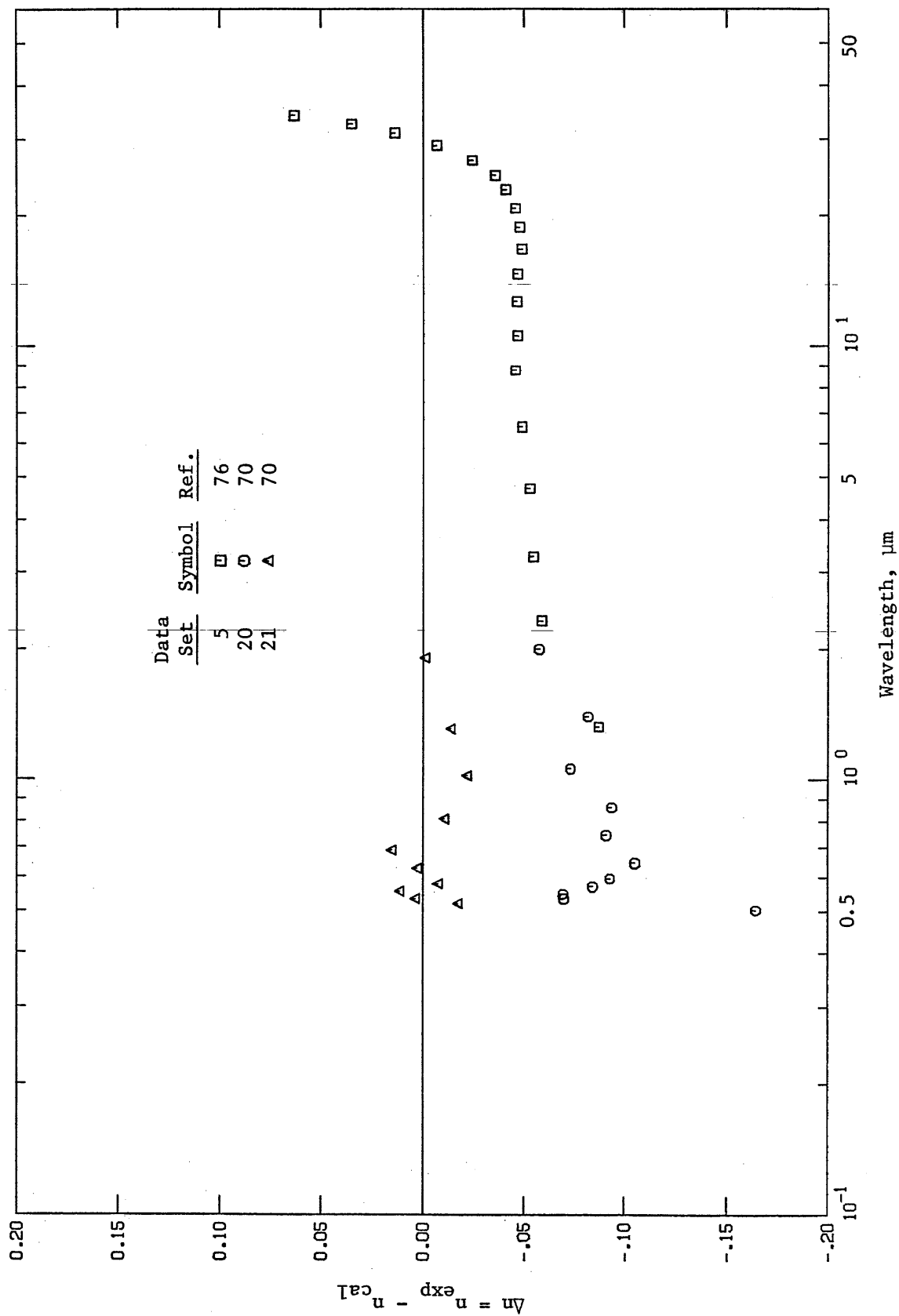


Figure 24. Comparison of experimental refractive indices of ZnTe films and calculated values for bulk ZnTe from Eq. (24). The calculated values are represented by the line  $\Delta n = 0$ .

Table 13. Recommended values on the refractive index and its wavelength derivative of ZnTe at 293 K

$\lambda$ , $\mu\text{m}$	$n$	$-\frac{dn}{d\lambda}$ , $10^{-3}\mu\text{m}^{-1}$	$\lambda$ , $\mu\text{m}$	$n$	$-\frac{dn}{d\lambda}$ , $10^{-3}\mu\text{m}^{-1}$
0.55	3.153	2902.4 <sup>a</sup>	13.5	2.670	4.8
0.60	3.040	1776.8	14.0	2.667	5.0
0.65	2.967	1189.7	14.5	2.665	5.2
0.70	2.917	846.0	15.0	2.662	5.4
0.75	2.880	628.4	15.5	2.659	5.7
0.80	2.853	482.3	16.0	2.656	5.9
0.85	2.831	380.0	16.5	2.653	6.2
0.90	2.814	305.6	17.0	2.650	6.4
0.95	2.801	250.1	17.5	2.647	6.7
1.0	2.789	207.7	18.0	2.643	7.0
1.5	2.736	53.0	18.5	2.640	7.3
2.0	2.719	21.6	19.0	2.636	7.6
2.5	2.711	11.3	19.5	2.632	7.9
3.0	2.706	6.9	20.0	2.628	8.2
3.5	2.704	4.8	20.5	2.624	8.6
4.0	2.701	3.7	21.0	2.620	8.9
4.5	2.700	3.1	21.5	2.615	9.3
5.0	2.698	2.8	22.0	2.610	9.7
5.5	2.697	2.7	22.5	2.605	10.1
6.0	2.696	2.6	23.0	2.600	10.5
6.1 <sup>b</sup>		2.6 <sup>b</sup>	23.5	2.595	10.9
6.5	2.694	2.6	24.0	2.589	11.4
7.0	2.693	2.7	24.5	2.584	11.9
7.5	2.692	2.8	25.0	2.577	12.4
8.0	2.690	2.9	25.5	2.571	12.9
8.5	2.689	3.0	26.0	2.565	13.5
9.0	2.687	3.1	26.5	2.558	14.1
9.5	2.686	3.3	27.0	2.550	14.7
10.0	2.684	3.4	27.5	2.543	15.3
10.5	2.682	3.6	28.0	2.535	16.0
11.0	2.680	3.8	28.5	2.527	16.8
11.5	2.678	4.0	29.0	2.518	17.5
12.0	2.676	4.2	29.5	2.509	18.4
12.5	2.674	4.3	30.0	2.500	19.2
13.0	2.672	4.6			

<sup>a</sup>The uncertainties of  $dn/d\lambda$  (in units of  $10^{-3}\mu\text{m}^{-1}$ ) are:  $\pm 2$  at 0.7  $\mu\text{m}$ ,  $\pm 2$  at 1  $\mu\text{m}$ ,  $\pm 4$  at 5  $\mu\text{m}$ ,  $\pm 2$  at 10  $\mu\text{m}$ , and  $\pm 1$  in the range 15 to 30  $\mu\text{m}$ .

<sup>b</sup>Minimum point on the  $dn/d\lambda$  curve.

#### 4. Discussion and Conclusions

Experimental data on the refractive index of zinc chalcogenides and its temperature derivative have been reviewed and recommended values of these materials were generated. The state of art of the refractive index of each of these materials is not well defined and our recommendations should be considered at best the average values of selected data sets. Many factors are known to influence the accuracy of refractive index determinations. The two most important are the measurement technique and the specimen characteristics. Although the minimum deviation method is known to be the most accurate way of determining the refractive index and in many cases these are reported to the fourth or fifth decimal place, its reproducibility is applicable only for a given specimen on a given setup of apparatus. For different specimens, even from the same batch, the reproducibility of this method is significantly reduced as the properties of the materials are influenced by many factors which are especially important in the semiconductors. Among other things, the single most important factor is the impurity content of the specimen. Although this is a well-known source of error, unfortunately, this very piece of information is usually not reported. As a consequence, discrepancies among the available data cannot be reasonably resolved.

The empirical dispersion equations, Eqs. (21) and (23), used to generate recommended values of ZnS and ZnSe are both wavelength and temperature dependent. At a given temperature, the wavelength-dependent equation is reduced to a Sellmeier-type formula widely used to represent refractive index in the fundamental transparent region. At a given wavelength, however, the temperature dependence is simply a fourth degree polynomial function of temperature. This is done because of a lack of reliable data over a wide wave-

length and temperature range and the lack of an understanding of the real physical processes affecting the optical properties of these materials. The majority of reported  $dn/dT$  measurements have centered on a temperature region around the room temperature which is, coincidentally, a temperature range over which the  $dn/dT$  is least dispersive. As a result, all reports commonly assume that, within the experimental error,  $dn/dT$  does not vary with temperature. Such observations are misleading and the consequence is that most theoretical studies interpreting  $dn/dT$  data underestimate the contributions from lattice mechanisms. Contributions to  $dn/dT$  (in the transparent region) from lattice are not negligible and variation of phonon occupation number is not properly accounted for. In reality, however,  $dn/dT$  does vary appreciably with temperature and the lattice term does have significant contribution particularly at long wavelengths, 10.6  $\mu\text{m}$ , for example, as discussed in the cases of ZnS and ZnSe. Referring to Figs. 6 and 16, the monotonic increase of  $dn/dT$  with increasing temperature in the region  $> 400$  K is real as supported by the available data. The physical mechanism of such behavior is not known; perhaps the theory of multiphonon process may shed light to what really happens. Presently, such theoretical treatments do not exist and the  $n$  and  $dn/dT$  data can only be best presented by the polynomial functions proposed in this work.

It should be pointed out that the dispersion equation proposed in this work reflects both the refractive index and the  $dn/dT$  data; in other words,  $n$  and  $dn/dT$  maintain a relationship in integration and differentiation. Depending on the quality and type of available data, the constants in the dispersion equation can be determined through either expression. As a contrast, other investigators have treated  $n$  and  $dn/dT$  data separately, describing each by an equation with a different starting point. As a result, there is no bridge between  $n$  and  $dn/dT$  expressions.

It should be noted that the present work relies heavily on the highly accurate data of Feldman *et al.* The present situation is unsatisfactory and not enough data exist covering a sufficient range of temperature for all applications and theoretical studies. A serious attempt should be made to carry out a systematic measurement program with the following considerations:

(1) Experimental method. The minimum deviation method is not suitable for the determination of a highly accurate refractive index at either high or low temperatures and it is strongly felt that the counting of interference fringe shift as a function of temperature should yield much better results. In this method, the sensitivity depends on the order of interference. In order to obtain high accuracy, thick plate specimens should be used.

(2) Sample characterization. The impurity content of the sample strongly affects the refractive index. Consequently, the impurity level in the sample must be ascertained and reported. Merely reporting the electrical resistivity or carrier concentration of the sample is not adequate. The nature and amount of impurities should specifically be reported. Measurements should be carried out for a group of specimens with systematically controlled impurities.

(3) Environmental control. Since the temperature coef-

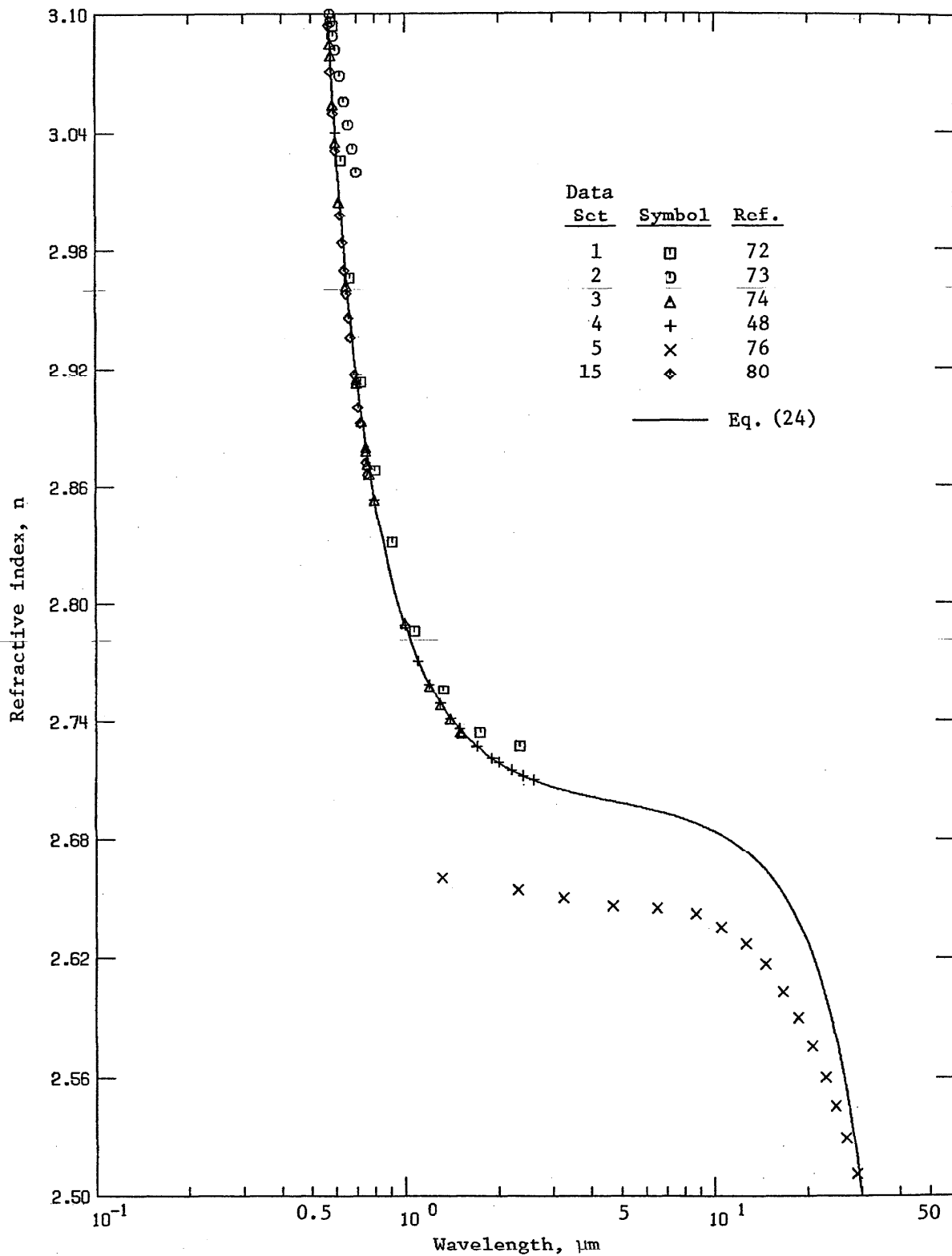


Figure 25. Recommended refractive index of ZnTe at 293 K.

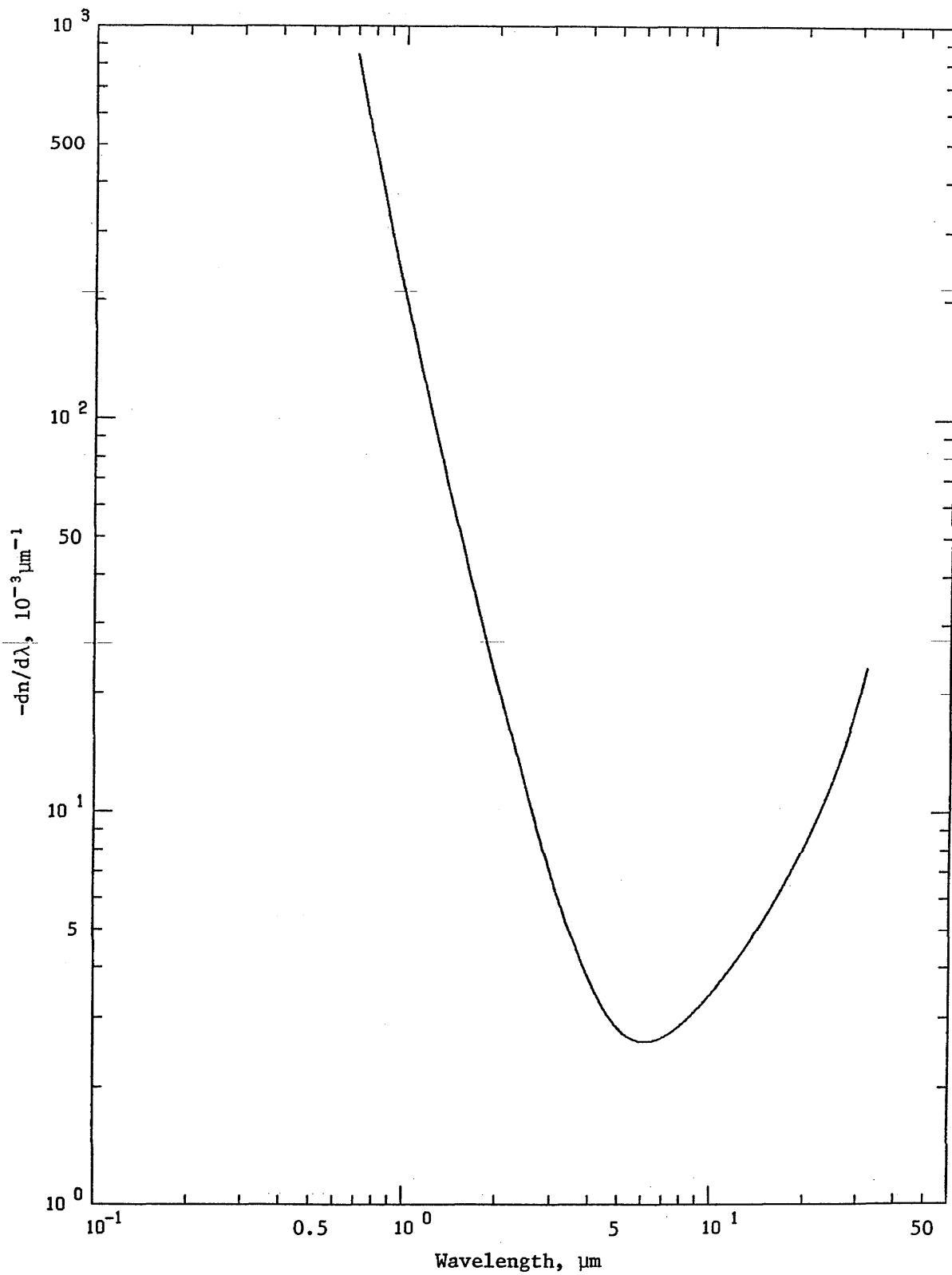


Figure 26. Recommended  $dn/d\lambda$  curve of ZnTe at 293 K.

ficient of refractive index of zinc chalcogenides are rather high, in the order of  $5 \times 10^{-5}$  to  $10^{-4} \text{ K}^{-1}$ , the temperature of the sample must be carefully controlled to achieve the required accuracy.

In conclusion, it should be emphasized that the present work does not resolve the discrepancies among the available data sets, it simply recommends the most probable values of the refractive index for pure ZnS, ZnSe, and ZnTe with the quoted uncertainties. Also, it should be noted that, as in any statistical study of this type, the dispersion equations, Eqs. (21), (23), and (24), are valid to the reported accuracy only within the region of experimental data. In general, extrapolation of these equations for use outside of this region is invalid for quantitative results. Finally, the type of analysis presented here assumes the model is a correct representation of the data. This is not generally true since the model is an oversimplification of the true dispersion relation. However, for predictive purposes, based upon the experimental data from several authors, and within the usable region of the data, we believe that these equations are valid for calculation of the refractive index in the given wavelength and temperature regions.

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