

# CRYSTAL GROWTH MECHANISM IN CORDIERITE AND DIOPSIDE GLASSES IN WIDE TEMPERATURE RANGES

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We measured and collected literature data for the crystal growth rate,  $U(T)$ , of  $\mu$ -cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) and diopside ( $\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$ ) in isochemical parent glasses. The numerous data obtained cover exceptionally wide temperature ranges, *i.e.* 800 - 1350°C for cordierite and 800 - 1392°C for diopside. The maximum of  $U(T)$  is reached at about 1250°C for both systems and smooth shoulders occur at  $\approx 1025^\circ\text{C}$  and  $\approx 970^\circ\text{C}$  for  $\mu$ -cordierite and diopside, respectively. Based on measured and collected viscosity data,  $U(T)$  could be fitted in terms of standard crystal growth models. The experimental crystal growth data of both systems can be fitted with the 2D surface nucleation growth model as well as with the screw dislocation model, but, for diopside, fitting with the latter model leads to more meaningful physical parameters. Especially for  $\mu$ -cordierite, it is necessary to separate the mean interatomic distance in the melt,  $\lambda$ , and the size of the building unit,  $d$ . Good fitting is possible only for very small  $\lambda$  (of the order of magnitude of the oxygen ion radius). The best fittings, which included the shoulders in  $U(T)$ , were accomplished for combined mechanisms, *i.e.* assuming that the melt/crystal interface, covered by screw dislocations, is additionally roughened by superimposed secondary crystals (formed by 2D surface nucleation), specially at temperatures around the observed shoulder and below.

(Key words: cordierite, diopside, glass, crystal growth)

## 1 Introduction

Knowledge of the temperature dependences and magnitudes of crystal growth rates in glass-forming liquids are of technological and fundamental interest. For isochemical crystallization, crystal growth rates have been widely described in terms of standard models of interface-controlled growth (*e.g.* [1,2]) assuming different mechanisms, such as *normal growth*, *screw dislocation growth* or *2D nucleated growth*. Most studies of crystal growth are restricted to temperature ranges of 200 to 300 K below the melting temperature,  $T_m$ .

In one study of crystal growth in *wide* temperature range, Burgner and Weinberg [3] collected growth rates of internally nucleated lithium disilicate crystals in  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glasses between  $T_g$  and  $T_m$ . They have suggested that such crystal growth rates over broad  $\Delta T$  ranges may be described by different growth mechanisms and that the usual phenomenological laws are applicable only in limited temperature regimes. Meanwhile, crystal growth rate data for two other silicate glasses have been measured in similar broad temperature ranges. Thus, extensive studies on surface nucleated crystallization of high-quartz solid solution crystals, denominated here as „ $\mu$ -cordierite“ ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) in cordierite glasses [4-8] would allow analogous data analysis. As another case of surface nucleated crystallization, the crystal growth rates of *diopside* ( $\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$ ) were comprehensively studied [9,10]. In addition, thermodynamic and kinetic data, such as melting enthalpy and viscosity as a function of temperature are available for both systems, which facilitates quantitative comparisons between theory and experiment.

It is the aim of the present work to summarize all collected and measured growth rate data for  $\mu$ -cordierite and diopside crystals in isochemical melts, in a broad temperature range, and to discuss their observed temperature dependence in light of classical theoretical models.

## 2 Experimental

*Glasses:* Most of the presented crystal growth data refer to glasses of nominal composition of cordierite 51.3 SiO<sub>2</sub>, 34.9 Al<sub>2</sub>O<sub>3</sub>, 13.8 MgO (wt%), and diopside 18.6 MgO, 25.9 CaO, 55.5 SiO<sub>2</sub> (wt%) (the authors added 1 wt% Al<sub>2</sub>O<sub>3</sub>). We melted all glasses from reagent grade raw materials in air, in Pt-crucibles. Plates of  $\approx 10 \times 15 \times 1$  cm<sup>3</sup> were prepared by casting the melts onto steel plates and slowly cooling to room temperature. Chemical analysis of the quenched glasses showed that no oxide component deviates more than 0.8 wt% from the nominal composition.

*Viscosity:* Low temperature data for cordierite and diopside melts were obtained from a beam-bending viscosimeter, and high temperature data by rotational viscosimetry.

*Crystal growth rate:* All crystal growth rate measurements for  $\mu$ -cordierite were performed using bulk pieces of glass ( $\approx 5 \times 5 \times 5$  mm<sup>3</sup>). Most of the thermal treatments were performed in atmosphere of  $\approx 20$  % relative air humidity (dew point  $\approx 8.5$  °C).

Different techniques were used to measure the crystal growth rates of  $\mu$ -cordierite at low and high temperatures. Below 830°C, we measured the further growth of pre-existing crystals by means of electron or optical microscopy (increase of the maximum radius of selected surface crystals). Between 830°C and 920°C, the maximum radius of crystals grown during one-step crystallization treatments were measured. Above 1000°C, the thickness of the crystalline surface layer was obtained. Between 900 and 1050°C both methods were applied. In the case of *diopside*, the authors measured single crystals. Crystal layers were measured in [9,10] using hot stage microscopy.

## 3 Data Analysis

In terms of standard crystal growth models [1,2,11], the interface-controlled crystal growth rate,  $U(T)$ , is given by Eq. 1, where  $d$  is the size of the building units and  $Z(T)$  their impingement rate in m<sup>-2</sup>s<sup>-1</sup>,  $f(T) \leq 1$  is the fraction of preferred growth sites at the interface,  $\Delta G(T)$  the bulk free energy change upon crystallization,  $R$  the gas constant,  $T$  the absolute temperature [1,11].

$$U(T) = f(T) \cdot Z(T) \cdot d^3 \cdot \left[ 1 - \exp\left(-\frac{|\Delta G(T)|}{RT}\right) \right] \quad (1)$$

According to Hoffman [12],  $\Delta G(T)$ , can be approximated by Eq. 2 where  $\Delta H_m$  is the molar heat of melting, and  $T_m$  the melting temperature:

$$\Delta G(T) = \Delta H_m \frac{(T_m - T)T}{T_m^2} \quad (2)$$

$Z(T)$  can be estimated from the melt viscosity,  $\eta(T)$ , assuming that the molecular motion required for crystal growth is similar to that involved in transport in the liquid (using the Stokes–Einstein equation),  $\lambda$  is the mean jump distance,  $k_B$  is Boltzmann's constant, and  $c \leq 1$  as a steric coefficient [1].

$$Z(T) = \left\{ c \cdot \frac{k_B T}{3\pi \cdot d^3 \cdot \lambda^2 \cdot \eta} \right\} \quad (3)$$

For  $f(T)$ , three phenomenological models are known [1,2]. (i) In case of *normal growth*, the crystal/melt interface is rough on atomic scale, *i.e.* every site allows the attachment of new building units, and  $f(T) = \text{const.} \approx 1$ . (ii) According to the *screw dislocation* model, the interface is smooth and growth takes place at screw dislocations.  $f(T)$  is expressed by Eq. 4 [1, 2], where  $\sigma$  is the specific surface energy of the melt-crystal interface,  $V_m$  is the molar volume of the crystal, and  $c_S$  is a constant.

$$f_{\text{screw}}(T) = c_S \cdot \frac{d\Delta G}{4\pi\sigma V_m} \quad (4)$$

(iii) In the 2D surface nucleated growth model, the surface is considered atomically smooth and growth occurs by the formation of 2-dimensional surface nuclei.  $f(T)$  is expressed by [1]:

$$f_{2D}(T) = c_{2D} \cdot \exp\left(\frac{-W}{k_B T}\right) \quad (5)$$

where  $c_{2D}$  is a constant and  $W = \pi d V_m \sigma^2 / \varepsilon \Delta G$  is the work of forming the critical 2D surface nucleus. Herein  $\varepsilon = 3$  denotes the large crystal case (growth of multi secondary nuclei on the surface of each primary large crystal) [1], which should apply for most cases.

(iv) Finally, a combined mechanism can be assumed if one realizes that the melt/crystal interface, which is already covered by screw dislocations, is additionally roughened by superimposed 2D surface nucleated crystals:

$$f_{combined}(T) = f_{2D}(T) + f_{screw}(T) \quad (6)$$

## 4 Results

*Viscosity:* The measured viscosity curve of liquid cordierite and diopside can be fitted in terms of the Vogel-Fulcher-Tamman equation:  $\log_{10}\eta = A + B/(T-T_0)$ , where  $\eta$  is given in Pa·s, and  $A = -3.97$ ,  $B = 5316$  K, and  $T_0 = 762$  K for cordierite glass; and  $A = -4.27$ ,  $B = 3961$  K, and  $T_0 = 751$  K for diopside glass.

*Crystal growth:* The measured data for crystal growth rate of  $\mu$ -cordierite in supercooled liquids of the same composition,  $U_c(T)$ , are shown in Fig. 2 together with literature data covering exceptionally wide temperature ranges. The maximum of  $U_c(T)$  is reached at  $\approx 1250^\circ\text{C}$ . A shoulder is observed around  $1025^\circ\text{C}$ . Crystal growth rate data of *diopside* in supercooled liquids of the same composition,  $U_d(T)$ , are shown in Fig. 3. As in Fig. 2, Fig. 3 covers a wide range of crystal growth rates.  $U_d(T)$  is maximal at  $1286^\circ\text{C}$  and shows a smooth shoulder at  $\approx 970^\circ\text{C}$ .

Whereas the  $U_d(T)$  data for diopside, taken from different authors, show remarkable reproducibility, much higher data scatter is evident for  $U_c(T)$ . This scatter can be, at least partially, attributed to the decisive influence of the relative humidity of the surrounding air. This effect was measured in [4,19], where  $U_c(T = 945^\circ\text{C})$  increased three-fold, from 0.2 to 0.6  $\mu\text{m}/\text{min}$  for increasing air humidity (dew points between  $-60$  and  $+25^\circ\text{C}$ ). Although, another source of data scatter may result from the different techniques used to obtain crystal growth rate data, *i.e.* by measuring the maximum radius of separate crystals or the thickness of the crystalline surface layer, this difference did not affect  $U_c(T)$  significantly. This finding is illustrated for  $\mu$ -cordierite in Fig. 1 left, where a large  $\mu$ -cordierite surface crystal is growing from a pristine vacuum-fractured glass surface (parallel to the paper plane). Its maximum radius is comparable to the thickness of the  $\mu$ -cordierite surface layer that grew from the perpendicular sample surface. However, these different data are not significantly different. Small deviations due to the different crystal orientation (factor  $< 2$ ) do not appear in the logarithmic scale of Fig. 2.

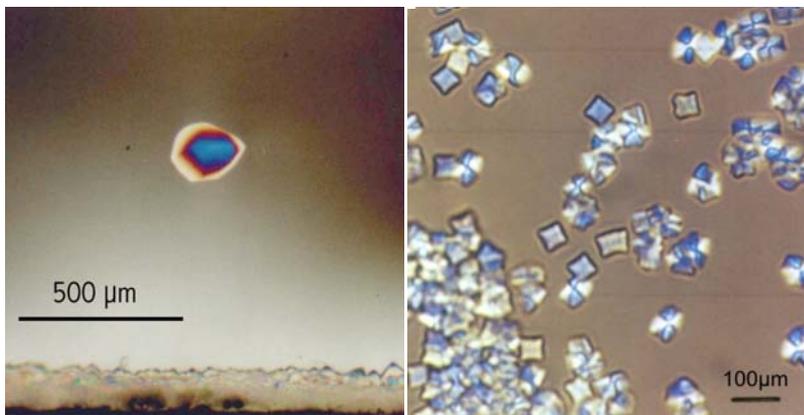


Fig. 1: *Left:* cordierite crystal and compact crystalline surface layer at a cordierite glass surface fractured and annealed ( $980^\circ\text{C}$ , 30 min) in vacuum. Transmitted light optical micrograph, top view, crossed nicols. *Right:* Diopside crystals at a polished diopside glass surface annealed in air ( $830^\circ\text{C}$ , 210 min). Transmitted light optical micrograph, top view, crossed nicols.

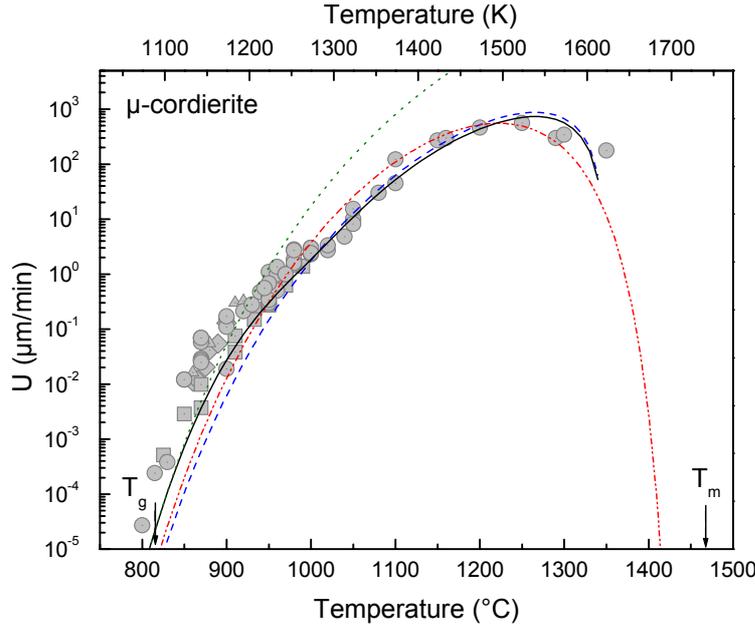


Fig. 2: Best fit of crystal growth rate data of  $\mu$ -cordierite in glass forming melts of the same composition by using each of the 3 models and the combined mechanism of crystal growth presented in section 3: normal growth: green dotted line, screw dislocation: blue dashed line, 2D surface nucleated growth: red dashed and dotted line, combined mechanism: black line. The used parameters are summarized in Table 1. Experimental points:  $\circ$ : this work ([4],[6]),  $\square$ : Yuritsin [5],  $\diamond$ : Hanay [15],  $\triangle$ : Diaz-Mora [7]

Table 1: Parameters used for fitting the experimental growth rate data of  $\mu$ -cordierite in Fig. 2.

Parameter	Normal growth	Screw dislocation	2D surface nucleated growth	Combined mechanism
$M$ (g/mol)	292	292	292	292
$T_m$ (°C)	1350	1350	1467	1350
$\lambda$ (m)	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$
$d = V^{1/3}$ (m)	$5.72 \cdot 10^{-10}$	$5.72 \cdot 10^{-10}$	$5.72 \cdot 10^{-10}$	$5.72 \cdot 10^{-10}$
$c$ (steric coefficient)	1	1	1	1
$\alpha$	-	0.4	0.34	0.8
$\sigma$ (J/m <sup>2</sup> )	-	0.192	0.163	0.384
$c_S$	-	3	-	5
$c_{2D}$	-	-	50	$5.2 \cdot 10^{13}$

*Crystal growth rate data analysis:*  $U(T)$  of both systems were fitted directly in terms of Eq.1-3 (*normal growth*), Eq. 1-4 (*screw dislocation*), Eq. 1-3, 5 (*2D surface nucleation*) or Eq. 1-6 (*combined mechanism*) (Fig. 2 and 3). Experimentally determined values of  $\eta(T)$  were used for  $\mu$ -cordierite and diopside. The melting point of  $\mu$ -cordierite  $T_m^c$  is uncertain due to the metastable nature of  $\mu$ -cordierite.  $T_m^c$  was estimated to be between 1300°C and 1467°C, the melting point of Indialite [13]. The cordierite melting enthalpy,  $\Delta H_m^c$ , is approximately 95 kJ/mol by estimating a building unit with  $M = 292$  g/mol ( $\approx 1/2$  formula unit) [13], and for diopside,  $\Delta H_m^d$  is near 138 kJ/mol [14].

The best results of direct fitting using all crystal growth models for  $\mu$ -cordierite and diopside are shown in Fig. 2 and Fig. 3, respectively.

*$\mu$ -cordierite:* *Normal growth* does not fit the experimental data, except at lower temperatures (green dotted line in Fig. 2). Using the *screw dislocation* model, the experimental data above 1000°C can be fitted well when for the metastable  $\mu$ -cordierite  $T_m^c = 1350^\circ\text{C}$  is assumed (blue dashed line in Fig. 2). The results for higher  $T_m^c$  are markedly worse (not shown). For  $T < 1000^\circ\text{C}$  the deviation from experimental points is up to 2 orders of magnitude. If  $T_m^c = 1467^\circ\text{C}$  is used, the *2D surface nucleated growth* model also fits experimental points fairly well (red dashed and dotted line in Fig. 2). But in the lower temperature regime ( $T < 900^\circ\text{C}$ ) the deviation reaches 1 order of magnitude. The best fit is obtained using the *combined mechanism*. By assuming the highest surface energy,  $\sigma$  (from Table 1) and  $T_m^c = 1350^\circ\text{C}$  it is possible to fit the smooth shoulder at 1000 – 1050°C (black line in Fig. 2).

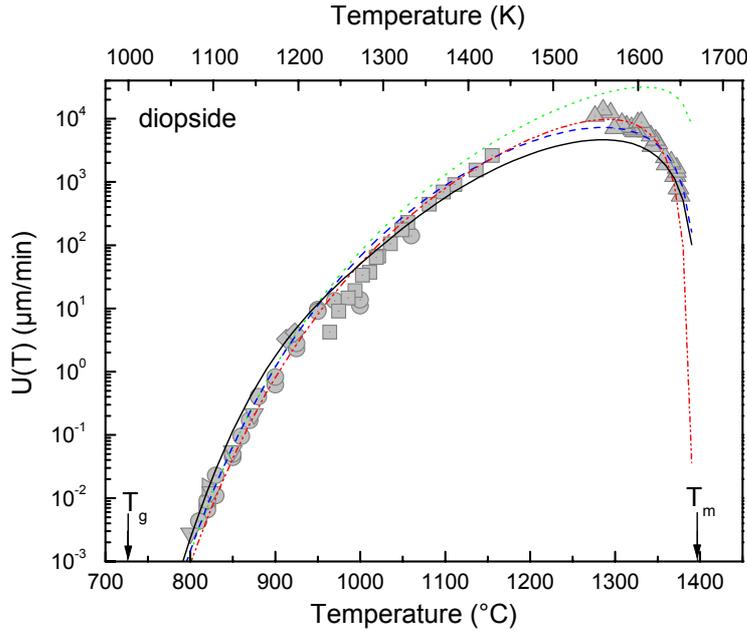


Fig. 3: Best fits of crystal growth rates of diopside in liquids of the same composition by using each of the 3 models of crystal growth, and the combined mechanism presented in section 3: normal growth: green dotted line, screw dislocation: blue dashed line, 2D surface nucleated growth: red dashed and dotted line, combined mechanism: black line. The used parameters are summarized in Table 2. Experimental points:  $\circ$ : Reinsch [4],  $\diamond$ : Nascimento [16],  $\triangleright$ : Zanotto [17],  $\triangle$ : Kirkpatrick *et al.* [10],  $\square$ : Briggs *et al.* [9],  $\nabla$ : Fokin & Yuritsin [18].

Table 2: Parameters used for fitting the experimental growth rate data of diopside in Fig. 3. \*: Different surface energies for screw dislocation (left) and 2D nucleated growth (right) part is assumed.

Parameter	Normal growth	Screw dislocation	2D surface nucleated growth	Combined mechanism
$M$ (g/mol)	216	216	216	216
$T_m$ (°C)	1397	1397	1397	1397
$\lambda$ (m)	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$	$1.32 \cdot 10^{-10}$
$d = V^{1/3}$ (m)	$4.79 \cdot 10^{-10}$	$4.79 \cdot 10^{-10}$	$4.79 \cdot 10^{-10}$	$4.79 \cdot 10^{-10}$
$c$ (steric coefficient)	0.003	0.07	0.07	0.03
$\alpha$	-	0.4	0.07	0.4 / 0.7 *
$\sigma$ (J/m <sup>2</sup> )	-	0.400	0.070	0.400 / 0.700 *
$c_S$	-	1	-	1.5
$c_{2D}$	-	-	0.04	$1 \cdot 10^{14}$

*Diopside*: Despite possible differences in glass preparation, impurity level and/or the methods employed for crystal growth measurements, all the data seem to be in accordance with respect to the magnitude and temperature dependence.

The *normal growth* model (green dotted line in Fig. 3) does not fit the experimental points very well except at  $T < 950^\circ\text{C}$ . With the *screw dislocation* model, the experimental data can be accurately fitted, except the smooth shoulder at  $950 - 1000^\circ\text{C}$  (blue dashed line in Fig. 3). Likewise, with the *2D surface nucleated growth* model the experimental points can be accurately fitted (red dashed and dotted line in Fig. 3). This fitting is only possible by assuming a very low surface energy,  $\sigma$  (see Table 2). Better fitting of the smooth shoulder is only possible by using the *combined mechanism* (black line in Fig. 3). Here, we had to assume two different surface energies,  $\sigma$ , for  $f_{screw}$  and  $f_{2D}$  (see Table 2).

## 5 Discussion

In crystal growth literature it is predominantly assumed that the mean jump distance,  $\lambda$ , can be equated with the size of the building unit  $d$  (Eq. 3). The latter can be estimated from the volume of a building unit ( $V = V_m/N_a$ ):  $d = V^{1/3}$ . Especially for  $\mu$ -cordierite, it was not possible to fit the experimental points with this assumption. Only for  $\lambda < d$ , an acceptable fitting was possible. So we used the smallest possible value for  $\lambda \approx 0.13$  nm (radius of oxygen ion), and  $d = V^{1/3}$  ( $d_c \approx 0.57$  nm,  $d_d \approx 0.48$  nm; see Tabs. 1 and 2). To realize a good fitting even in the lower temperature region near  $T_g$  with these

models a substantial lower  $\lambda$  is necessary. Generally, the temperature dependence of these models is in good agreement with the experimental data, even in the glass transition region.

The fittings in Fig. 2 and 3 were first done with no regards to the physical sense of the parameter  $\alpha$ , which relates to the value of  $\sigma$ . Literature values between 0.4 and 0.6 are common for measurable homogeneous (primary) nucleation in silicate glasses [20]. Thus, in the case of cordierite glass, the fitted values of 0.4 and 0.34 for screw dislocation and 2D nucleated growth, respectively, and in case of diopside, the value of 0.4 for screw dislocation growth are plausible. For fitting the combined mechanism for  $\mu$ -cordierite we have to set  $\alpha = 0.8$ . In the case of diopside glass, the 2D nucleated growth model forces one to assume a very small value of  $\alpha$ . But all known data of surface energy for silicate systems are determined indirectly from primary homogeneous nucleation experiments by use of the classical nucleation theory, with all its well-known discrepancies. In the case of the combined growth model for diopside, we used two different surface energies for  $f_{screw}$  and  $f_{2D}$  in Eq. 6. It may be possible that differences of surface energy on different points of the crystal surface are real (at the step of a dislocation or on the flat surface). Due to the indefiniteness of the melting point of  $\mu$ -cordierite  $T_m^c$  we have used  $T_m^c = 1350^\circ\text{C}$ . Even lower values have been used, for instance, in ref. [21] where experimental growth data of  $\mu$ -cordierite in a cordierite glass with addition of 8.1 wt%  $\text{TiO}_2$  were fitted with  $T_m^c = 1150^\circ\text{C}$ .

As an interesting feature of the present studies, smooth shoulders appear at  $\approx 1025^\circ\text{C}$  and  $\approx 970^\circ\text{C}$  for cordierite and diopside, respectively. A similar effect seems to occur in lithium disilicate at  $\sim 600^\circ\text{C}$  [3]. The observed slight shoulder in both systems can be roughly fitted in terms of combined mechanisms. Thus, other explanations, such as changes of crystal morphology, as observed by Diaz-Mora [7] near  $950^\circ\text{C}$  for  $\mu$ -cordierite, and the possible decoupling between diffusion coefficients and viscosity at  $\sim 1.2 T_g$ , are possible and will be discussed at length elsewhere [22].

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