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## OPTICAL ABSORPTION IN IRRADIATED NATURAL BERYL

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ABSTRACT

Three species of beryl irradiated with  $\gamma$ -rays of  $^{60}\text{Co}$  were studied by optical absorption. One became yellow and the other two Maxixe's blue. The effects of heat treatments were determined by the thermal isochronal decays of the optical absorption bands. Activation energies and frequency factor were obtained through the first order process kinetic model. Discussions lend us to assign for the UV band-edge the model of absorption by a hole center stabilized by a  $\text{Fe}^{2+}$  (substituting  $\text{Al}^{3+}$ ) ion in a neighbour oxygen.

INTRODUCTION

The non-chromian beryl is found in nature in several colours: colourless, yellow, green and blue. The colourless beryl turns yellow, Maxixe's green and Maxixe's blue by  $^{60}\text{Co}$   $\gamma$ -rays irradiation (Sinkankas, 1972). The yellow hue arises from the UV band-edge. The Maxixe's blue is due to the absorption band assigned to  $\text{CO}_2^-$  radical (Wood and Nassau, 1968). The green is a combination of the yellow and blue hues.

The UV band-edge shifts to shorter wavelengths on heating. By the end of such treatment the beryl turns colourless. On heating between  $100^\circ\text{C}$  and  $200^\circ\text{C}$  the Maxixe's blue colour is bleached leaving the sample yellow (Nassau et al., 1976).

It is our purpose to report the isochronal decay determined for yellow and Maxixe's blue colors induced in colourless beryl from Minas Gerais, Brazil, with  $\gamma$ -rays of  $^{60}\text{Co}$ .

EXPERIMENTAL

We studied in this report three samples of colourless beryl: A) colourless beryl obtained in the crystalline eyes from great stones in beryl ore prospection; B) crystals with hexagonal morphology, with faces of about  $1\text{cm}^2$  of area and 5 cm of height; C) morganite supplied by Halba Indústria e Comércio.

The thermal treatments were done in a FORLABO oven with heating chamber of  $10 \times 12 \times 15\text{cm}^3$ . The stability of this oven was improved to about  $\pm 2^\circ\text{C}$  by the introduction of brick materials and two metallic plates. The samples were heated between these plates. The thermalization curve for  $400^\circ\text{C}$ , obtained in a

1 cm<sup>3</sup> sample, with a chromel-alumel thermocouple inside the sample and a ECB XT recorder is sketched in figure 1. This shows

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Insert Figure 1

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that the thermalization time is lesser than 40 seconds, and is very reproducible.

The samples were cut to obtain 5 mm thick plates with a 0.012" thick low density diamond saw in a Isomet system from Buehler and polished using 180; 320; 400 and 600 abrasive papers, consecutively, and after we used alumina in a Minimet polishing system from Buehler.

Optical absorption spectra were obtained using a Carl Zeiss DMR 21 spectrometer.

The samples were irradiated with <sup>60</sup>Co γ-rays in the source of the EMBRARAD S/A at doses of about 4 MGy.

The isochronal heat treatment were done in the following way: the sample was treated in the oven by 10 minutes between the metallic plates. After that the sample was cooled between two other metallic plates at room temperature and then the optical absorption spectrum was obtained. The temperature was raised successively from one treatment to another.

## RESULTS

Sample A:- Irradiation induces yellow colour. In figure 2 we show the absorption spectra obtained for a sample ir

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Insert Figure 2

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radiated and then submitted to isochronal heat treatment. We see a band around 12,000 cm<sup>-1</sup> and a UV band-edge raising from 20,000 cm<sup>-1</sup>. The UV band-edge decays on heating from 166°C. The 12,000 cm<sup>-1</sup> band increases on heating from 246°C.

In figure 3 we show the isochronal growth of the

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Insert Figure 3

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12,000 cm<sup>-1</sup> band and the isochronal decay of the UV band-edge. We determined the UV band-edge decay through the decay of the absorption at 25,000 cm<sup>-1</sup>. The absorbances of both bands were normalized to the respective absorbances in the unheated sample.

Sample B:- Irradiation induces a deep blue Maxixe's type colour along the c-axis. In figure 4 we show the absorption

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Insert Figure 4

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spectra obtained for a sample irradiated and then submitted to isochronal heat treatment. We see a band around 12,000 cm<sup>-1</sup>, another around 14,000 cm<sup>-1</sup> with fine structure and a UV band edge raising from 22,000 cm<sup>-1</sup>.

In figure 4 we also show the result of the isochronal treatment in the optical absorption in beryl B. The UV band-edge decays revealing two bands, at 23,500 cm<sup>-1</sup> and 27,000 cm<sup>-1</sup>. These two bands appears to suffer neither irradiation nor thermal effects.

The isochronal decay of the 14,000 cm<sup>-1</sup> band is shown in figure 5. We see that a significative decay occurs at 150°C.

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Insert Figure 5

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Sample C:- Irradiation induces a deep blue colour. In figure 6 we show the absorption spectra obtained for a sample

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Insert Figure 6

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irradiated and then submitted to isochronal heat treatment. Here we notice the absence of the  $12,000\text{ cm}^{-1}$ ,  $23,500\text{ cm}^{-1}$ ,  $27,000\text{ cm}^{-1}$  and the UV band-edge observed in samples A and B. We see a band at  $14,000\text{ cm}^{-1}$  with hyperfine structure similar to that observed in sample B. A small band at  $34,000\text{ cm}^{-1}$  was also induced.

The isochronal decay of the  $14,000\text{ cm}^{-1}$  band is shown in figure 7. The thermal treatment effect is similar to that

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Insert Figure 7

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observed in sample B.

#### DISCUSSION

The band at  $12,000\text{ cm}^{-1}$  is due to  $\text{Fe}^{2+}$  in the crystal sites (Edgar and Vance, 1977; Goldman et al., 1977; Samoilovich et al., 1971; Wood and Nassau, 1968) and in the structural channels of beryl (Blak et al., 1982a). The isochronal growth of this band in yellow beryl (beryl A) is shown in figure 3. In colourless and pink beryl Blak et al. (1982a) showed that the kinetics of the growth of the  $12,000\text{ cm}^{-1}$  band does not obey simple first order kinetic process between  $200^\circ\text{C}$  and  $400^\circ\text{C}$ . As no theoretical expression for this kinetics were proposed we are not able to fit the isochronal curves obtained for the  $\text{Fe}^{2+}$  absorption.

The band at  $14,000\text{ cm}^{-1}$  is due to  $\text{CO}_3^-$  (Nassau et al., 1976; Edgar and Vance, 1977). The structure of this band is due to the electron-vibration interaction. The isochronal decay is shown in figures 5 and 7, respectively, for beryl B and C. Here we analysed this kinetics through the first order process kinetic model (Curie, 1963):

$$\frac{dn}{dt} = -s_0 n \exp(-\Delta E/kT) ,$$

where  $n$  is the number of  $\text{CO}_3^-$ ,  $s_0$  the frequency factor,  $\Delta E$  the activation energy,  $k$  the Boltzmann constant and  $T$  the absolute temperature. The solution of this equation is:

$$n = n_0 \exp[s_0 t \exp(-\Delta E/kT)] ,$$

where  $t$  is the heating time and  $n_0$  the initial number of  $\text{CO}_3^-$ . The intensity of absorption,  $I$ , is proportional to the number of  $\text{CO}_3^-$ , so  $I \propto n$ .

The parameter  $s_0$  and  $\Delta E$  were obtained by fitting the function:

$$\ln[\ln(I_{n-1}/I_n)] = \ln s_0 - \{\Delta E/k\} (1/T_n) .$$

The activation energy for both beryl B and C were found to be the same and of about 1 eV of magnitude. The frequency factors were different, of the order:

$$\text{beryl B} , s_0 = 28.3 \times 10^6 \text{ seg}^{-1} ,$$

$$\text{beryl C} , s_0 = 20.4 \times 10^6 \text{ seg}^{-1} .$$

The solid lines in figures 5 and 7 were evaluated using the above determined parameters.

In beryl B we found Fe as impurity, as shown in figure 4. On the other hand the beryl C contains negligible quantities of Fe as shown by the lack of  $\text{Fe}^{2+}$  absorption in figure 6. In beryl C the alkalides are the principal impurity (Blak et al., 1982b). In this way we conclude that the activation energy of  $\text{CO}_3^-$  is impurity independent. On the other hand the frequency factor is sensitive to impurities.

The process of inducing yellow colour by irradiation of colourless beryl and then bleaching the colour by heating is cyclic. The colour appear mainly due to the increasing the UV band-edge by irradiation and disappear by the bleaching of this band. So, the UV band-edge must be associated to deffects in crystal which can be filled and bleached.

In sample B, the  $12,000 \text{ cm}^{-1}$  and the UV band-edge appears while in sample C both bands are absent. So, the deffect associated to the UV band-edge must be correlated to the Fe content.

Let us examine the possibility of assign the UV band-edge to valence changes in Fe. The channel's  $\text{Fe}^{3+}$  ion is reduced into  $\text{Fe}^{2+}$  on heating. If the UV band-edge is due to channel's  $\text{Fe}^{3+}$ , its kinetics must be correlated to that of  $\text{Fe}^{2+}$ . However in figure 3 we show that the kinetics of  $\text{Fe}^{2+}$  absorption band ( $12,000 \text{ cm}^{-1}$ ) and of UV band-edge are not correlated. Also, the substitutional  $\text{Fe}^{3+}$  is not affected on heating.

The isochronal decay of the UV band-edge was fit using the first order process kinetic model, giving on activation energy of 0.16 eV and frequency factor  $6.8 \cdot 10^{-3} \text{ seg}^{-1}$ . These values are different of those obtained for  $\text{Fe}^{2+}$  absorption growth in beryl (Blak et al., 1982a).

From the above considerations we drop the hypothesis

that the colour changes in colourless beryl are associated with the process of valence changes in Fe.

Let us examine the possibility of assign the UV band-edge to the electron centers. These centers can be trapped in oxygens neighbour to Fe in such a site which it will be a positive charge deffect in the crystal. This is the case of Fe ions in the structural channels because in these sites Fe is not bonded to the neighbour oxygens. These oxygens ions are  $\text{O}^{2-}$  with all 2p orbitals occupied by electrons. So, electrons trapped in these oxygens must occupy 3s orbital. This will give a very shallow trap. Usually, electron centers trapped in these oxygens are unstable at room temperature (Marfunin, 1979).

The hole trapped in oxygen of the lattice, i.e.,  $\text{O}^-$ , is characterized by the absense of one 2p electron. In this case the hole center will be deeper trapped. Hole centers in irradiated silicate crystals are usually stable at temperatures higher than  $100^\circ\text{C}$  and are responsible by the darkening. For example, in quartz, a hole is trapped in oxygen neighbour to  $\text{Al}^{3+}$ . The substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  introduces a negative charge deffect in the lattice, which allows the capture of a hole.

The most common substitutional site of Fe in beryl crystal is  $\text{Al}^{3+}$ . The substitution of  $\text{Fe}^{3+}$  in the  $\text{Al}^{3+}$  site does not constitute a charge deffect. On the other hand the substitution of  $\text{Fe}^{2+}$  in the  $\text{Al}^{3+}$  site gives a negative charge deffect in the lattice.

From the above considerations we propose that irradiation of beryl produces  $\text{Fe}^{2+} - \text{O}^-$  centers. The UV band-edge is due to the absorption by holes trapped in oxygens, i.e., by the  $\text{O}^-$  ions, which are stabilized by neighbour negative charge deffects in the lattice due to the substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{2+}$ .

ACKNOWLEDGEMENTS

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## FIGURE CAPTIONS

Figure 1 - Thermalization curve of beryl.

Figure 2 - Optical absorption spectra of beryl A.

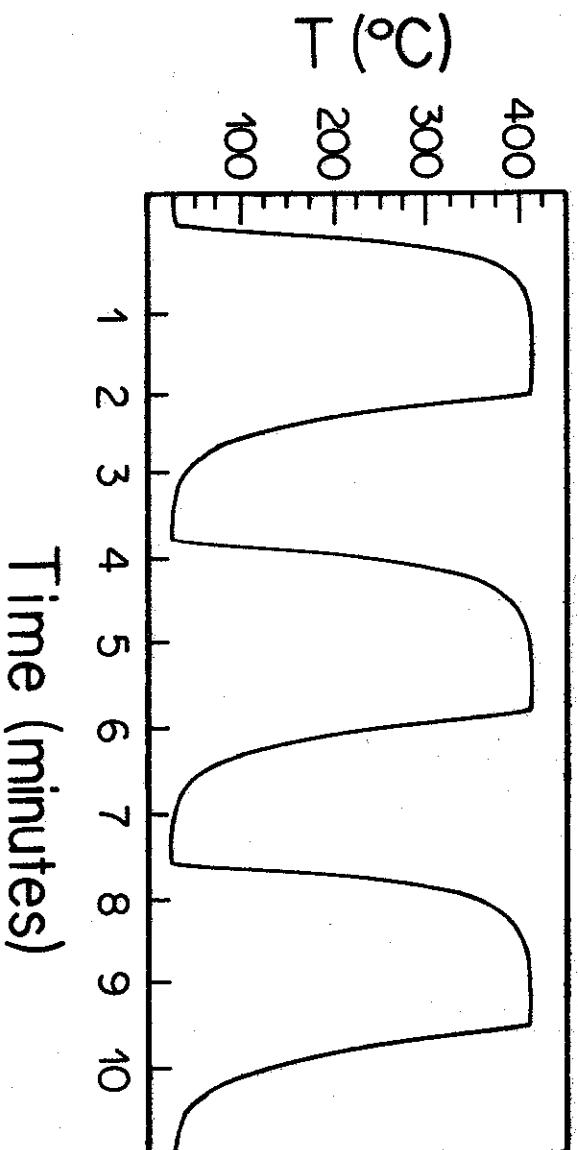
Figure 3 - Isochronal growth of the band at  $12,000 \text{ cm}^{-1}$  ( $\square$ ) and isochronal decay ( $\Delta$ ) of the UV band-edge at  $25,000 \text{ cm}^{-1}$  in beryl A. The solid line were evaluated using the first order kinetic model with activation energy  $0.167 \text{ eV}$  and frequency factor  $6.8 \cdot 10^{-3} \text{ seg}^{-1}$ .

Figure 4 - Optical absorption spectra of beryl B.

Figure 5 - Isochronal decay of the band at  $14,000 \text{ cm}^{-1}$  of beryl B ( $\bullet$ ). The solid line were evaluated using the first order kinetic model with activation energy  $1 \text{ eV}$  and frequency factor  $28.3 \cdot 10^6 \text{ seg}^{-1}$ .

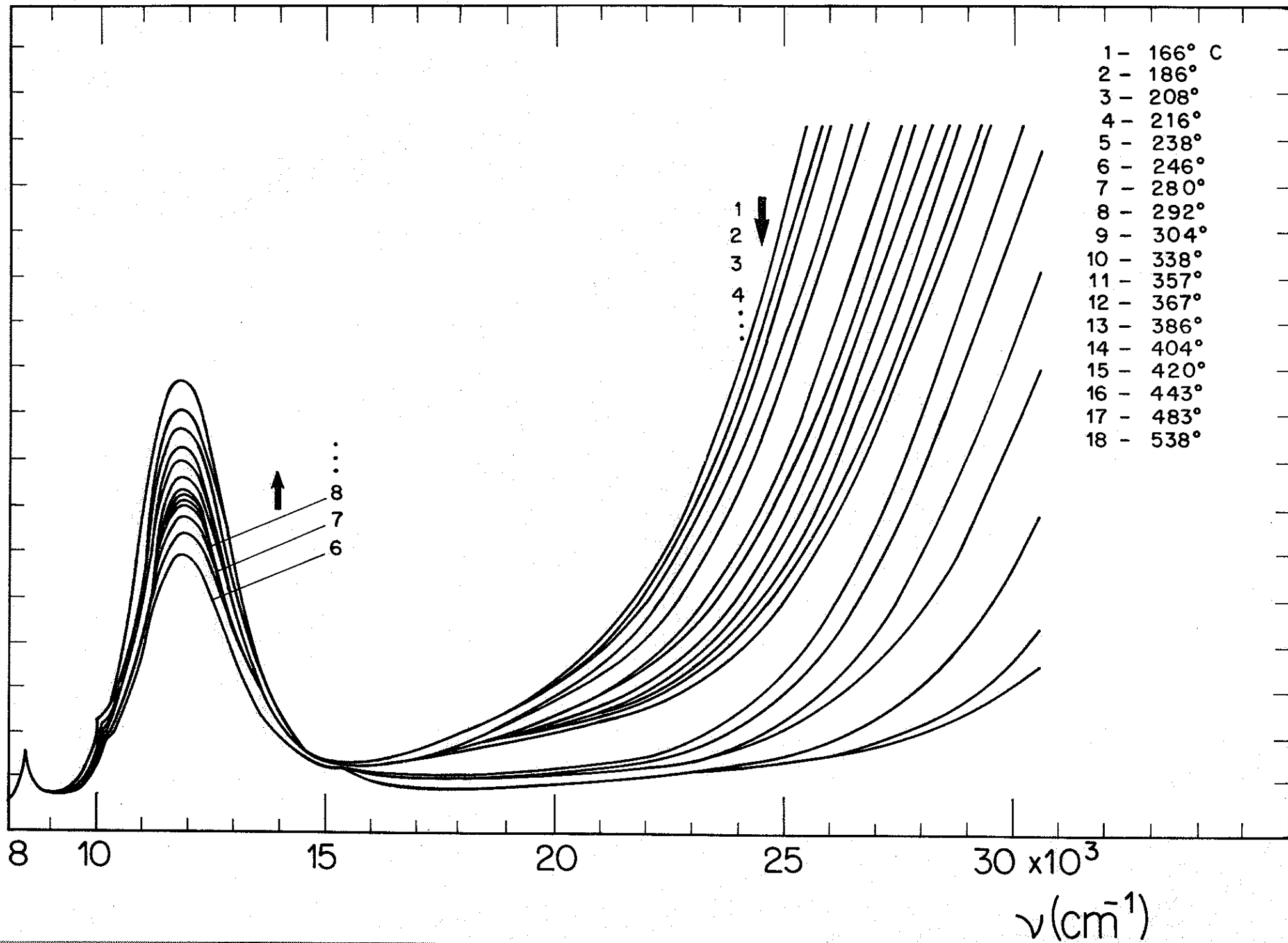
Figure 6 - Optical absorption spectra of beryl C.

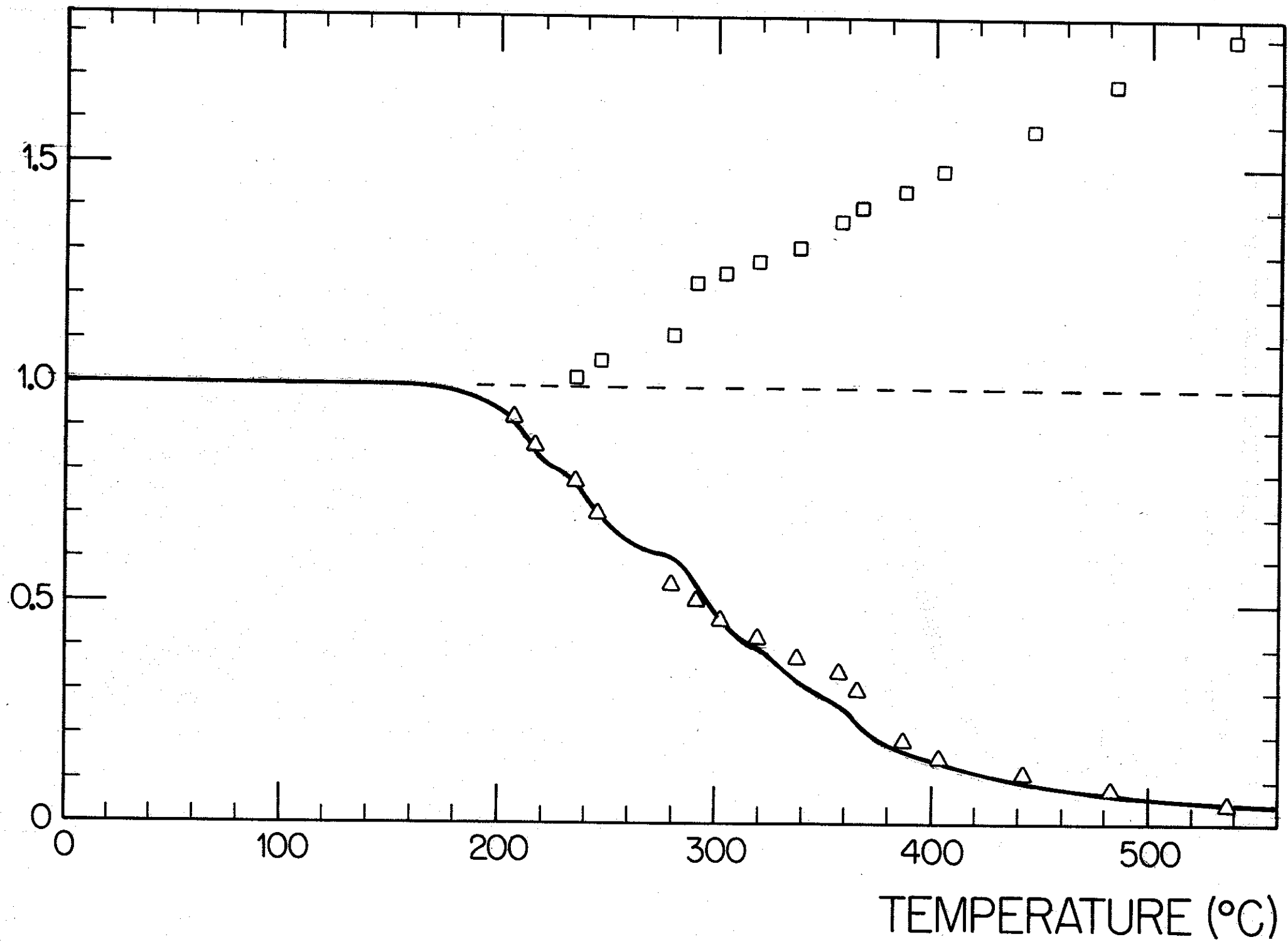
Figure 7 - Isochronal decay of the band at  $14,000 \text{ cm}^{-1}$  of beryl C ( $\bullet$ ). The solid line were evaluated using the first order kinetic model with activation energy  $1 \text{ eV}$  and frequency factor  $20.4 \cdot 10^6 \text{ seg}^{-1}$ .



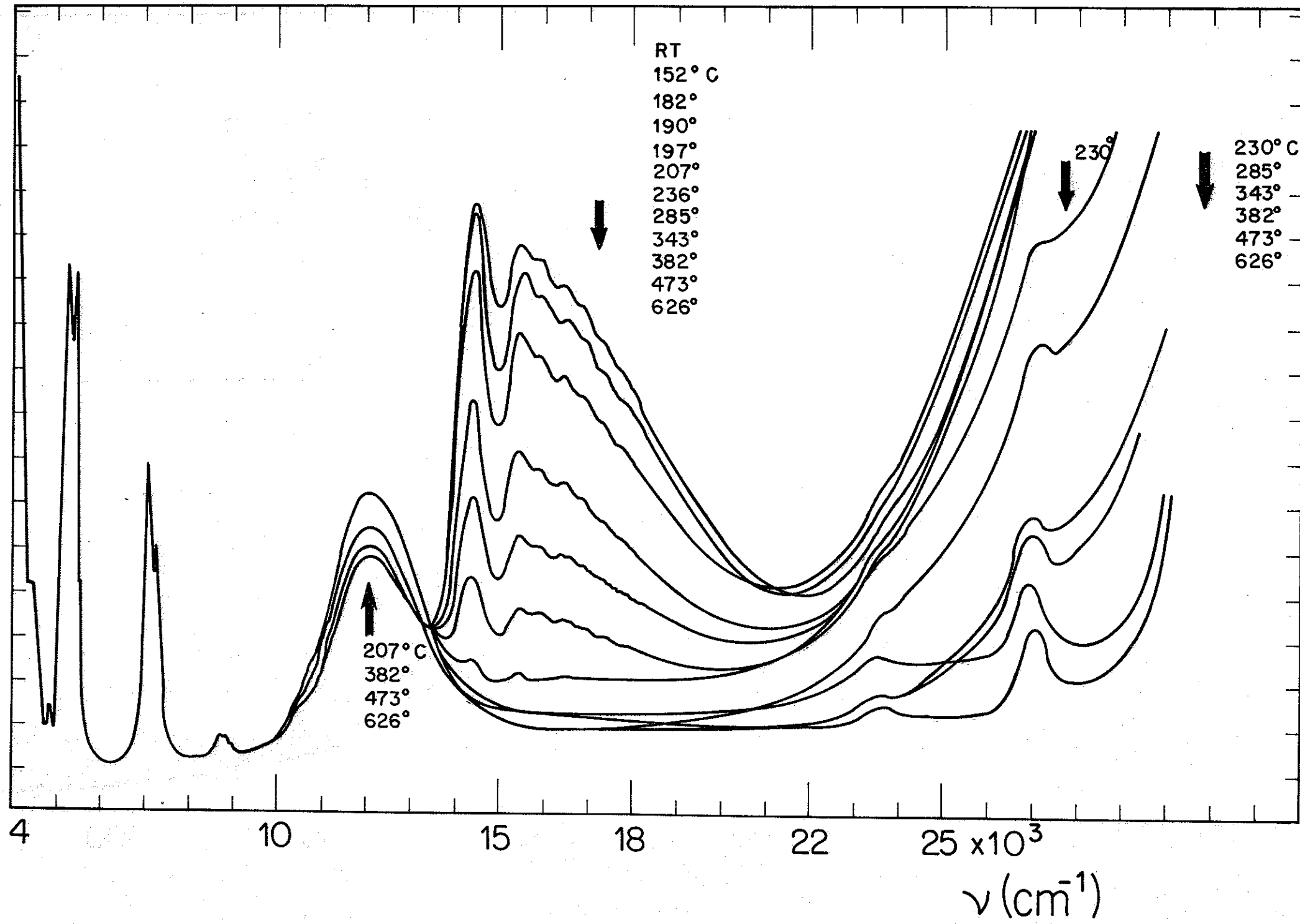


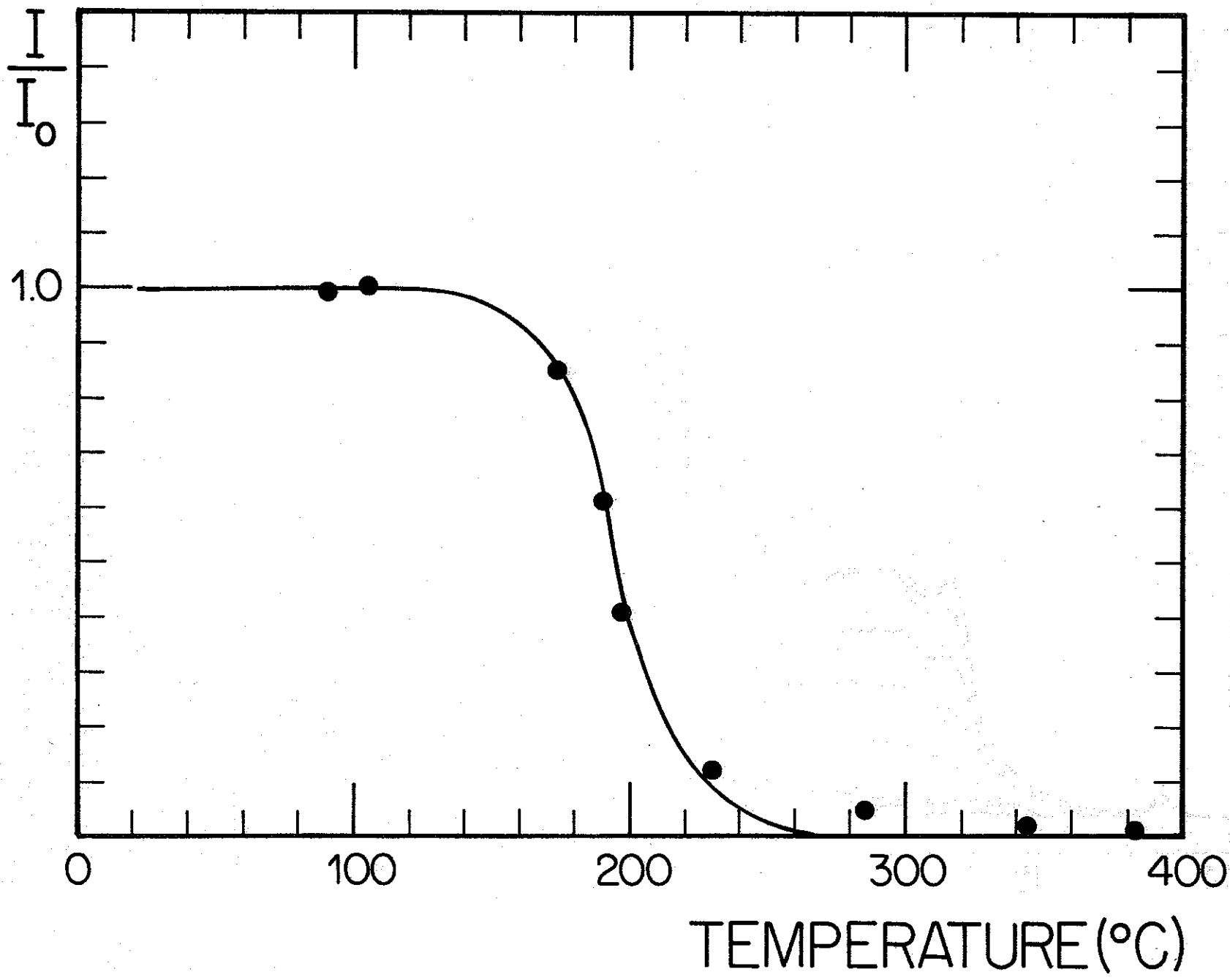
OPTICAL DENSITY (arbitrary scale)





Q. D.





O. D.

