



COLOR CENTERS IN CALCITE

by

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ABSTRACT

Coloration of pure crystals of calcite produces absorption bands at 290 and 350 $m\mu$. The band at 290 $m\mu$ which is anisotropic, absorbing only for the ordinary ray, has been attributed to color centers located in the carbonate groups, while the isotropic band at 350 $m\mu$ has been attributed to calcium color centers. To explain the fact that both bands bleach identically, and that an equal number of centers is associated with each band, it is proposed that the centers are produced in pairs by transferring an electron from a carbonate group to a calcium lattice position. In addition to these two bands, further coloration which may be due to a third band, is produced in the neighborhood of the fundamental absorption edge.

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INTRODUCTION

Due to their inherent structural simplicity and relatively easy preparation alkali halide crystals have been the subject of most color center research⁽¹⁾. Although considerable work has been done with these substances, the detailed nature of color centers is not well understood. More recently in an effort to gain further information, some of the more complicated structures have been investigated. Among these are the divalent halides such as CaF_2 ⁽²⁾ and several of the non cubic systems including quartz^(3,4) and corundum⁽⁵⁾.

Using samples of natural and synthetic quartz irradiated with x-rays, Cohen⁽⁴⁾ found an anisotropic absorption band centered at 460 μ . With polarized light a peak shift to 485 μ was observed for the ordinary ray (electric vector vibrating perpendicular to the c-axis). When the extraordinary ray (electric vector parallel to the c-axis) was used the peak was found at 460 μ . A second smaller peak present only for the extraordinary ray was also reported. These centers are believed^(4,6) to be associated with Al impurities replacing Si in the lattice. These band peaks were

(1) See F. Seitz, "Color Centers in Alkali Halide Crystals II, Rev. Mod. Phys. 26, 7, (1954)

(2) A. Smakula, Phys. Rev. 77, 408 (1950); 91, 1570 (1953)
A. Smakula, Z. Physik 138, 276 (1954)
W. Scouler and A. Smakula, Phys. Rev. 120, 1154 (1960)
D. Messner and A. Smakula, Phys. Rev. 120, 1162 (1960)

(3) A. Smakula, J. Opt. Soc. Am. 40, 266 (1950)

(4) A. F. Cohen, J. Chem. Phys. 25, 908 (1956)

(5) R. J. Hunt and R. H. Schuter, Phys. Rev. 89, 664 (1953)

found⁽⁴⁾ to saturate with absorption coefficients between 3.5 and 11 cm^{-1} depending upon the amount of Al present.

In a later series of experiments Cohen⁽⁶⁾ irradiated with x-rays samples of quartz containing Ge impurities as well as Al. He found an additional anisotropic band at 275 $\text{m}\mu$ with maximum absorption for the extraordinary ray.

Batrak⁽⁷⁾ measured the luminescence band of x-irradiated quartz and found a peak at 445 $\text{m}\mu$. In order to explain this effect he proposed that the Al impurities substituting for Si in the lattice actually act as activators playing a role similar to such impurities in ordinary phosphors.

Uncontaminated samples of quartz are very difficult to obtain, and there seems to be no mention in the literature about color centers in chemically pure quartz.

X-ray coloration of corundum (Al_2O_3) single crystals produces⁽⁵⁾ absorption bands at 400, 230 and 650 $\text{m}\mu$. The coloration due to these centers is relatively stable at room temperature for moderate periods of time, i.e. weeks, but is found to saturate after a very short exposure. An absorption coefficient of only 0.4 cm^{-1} is reported for the 400 $\text{m}\mu$ band.

Levy and Dienes^(8,9) irradiated corundum with gamma rays and with neutrons. Using gamma rays they obtained essentially the same results as described above.

(6) M. C. M. O'Brien, Proc. Roy. Soc. A231, 404-14 (1955)

(7) E. N. Batrak, Sov. Phys. Crystallog. 3, 633-4 (1958) (English translation)

(8) P. W. Levy and G. J. Dienes "Report of the Bristol Conference on Defects in Crystalline Solids", The Physical Society, London (1955), pp. 256-260

(9) G. J. Dienes and G. W. Vineyard "Radiation Effects in Solids", Interscience Publishers, New York (1954)

However, neutron irradiation was found to produce additional bands at 204, 260, and 165 μ . During irradiation the latter bands increased in intensity linearly at first, then more slowly at high levels of coloration. Levy and Dienes attributed the gamma coloration to ionizing effects, and the additional coloration produced by neutron bombardment to color centers resulting from displaced atoms. There seems to be no information available in the literature about the anisotropy of color centers in corundum.

Prigsheim⁽¹⁰⁾ found that absorption bands in NaNO_3 irradiated with x-rays resulted from two different effects. He was able to show that one band at 345 μ was produced by the conversion of the somewhat unstable NO_3^- ions into NO_2^- ions. An additional band at 335 μ which was easily bleached by ultraviolet light, he attributed to color centers. Although these color centers were easily bleached, he was able to find no photoconductivity associated with them. He concluded therefore that in the back reaction each trapped electron must move only through a very short distance in returning to its ground state. As in the case of corundum, no study of the anisotropy of these absorption bands was made.

As can be seen from the preceding, past investigations of color centers in non-cubic crystals have been for the most part complicated by the presence of chemical impurities, resistance to coloration, or chemical instability. In this study calcite was selected because large natural crystals of high purity and perfection were available. In addition, calcite is known to be highly anisotropic.

(10) P. Prigsheim, J. Chem. Phys. 23, 369 (1955)

EXPERIMENTAL PROCEDURE

Since calcite is readily cleaved into rhombohedrons the preliminary investigations were done on cleaved samples. After cleaving, the samples were ground and polished with "Linde A" to minimize surface scattering in the ultraviolet region.

To obtain samples oriented parallel to the c-axis, the following technique was used. Since the cleavage rhombohedron bears a definite relationship to the crystal lattice itself, it was possible to locate a plane containing the c-axis simply by bisecting one of the obtuse cleavage face angles, and cutting the crystal along this line perpendicular to the bisected surface. Samples produced in this manner were then ground and polished. To locate the actual c-axis direction in the now exposed plane a petrographic polarizing microscope was used. The procedure is described in standard textbooks on optical mineralogy⁽¹¹⁾. In order to check the results obtained by this method, Laue x-ray photographs of the samples were used.

To color the calcite samples the M.I.T. Van de Graaf accelerator was used to produce 3 Mev electrons. Using electrons for irradiation has the advantage that reasonably large (as much as 5×10^6 rads⁽¹²⁾) accurately controlled doses can be administered in a relatively short time. Usually only a few seconds are required as opposed to as much as several hours for conventional x-ray doses of similar magnitude. This is a distinct advantage especially if the centers produced are thermally unstable. The effects of 3 Mev electrons on atomic displacement production will be discussed later.

(11) see for example Rogers and Kerr "Optical Mineralogy", McGraw Hill Co.

(12) The rad is defined as an energy dose of 100 ergs per gram of material.

Optical absorption measurements were made with a Beckman model DK-1 spectrophotometer using an incandescent light source for the visible and long wave regions and a hydrogen lamp for the ultraviolet region. To obtain polarized light for anisotropy measurements a calcite air-gap prism was used.

In order to irradiate and measure the absorption of samples at -190°C a cryostat was used. This consisted of a vacuum chamber in which the sample was mounted and a container for liquid nitrogen to provide a low temperature. To insure opacity at all wavelengths the cryostat was provided with quartz windows.

PROPERTIES OF CALCITE

Calcite is a crystalline form of CaCO_3 belonging to the rhombohedral class ⁽¹³⁾, group D_{3d}^6 ($R \bar{3} c$). According to this classification it has atoms at the following positions:

$$\text{Ca} : \frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$$

$$\text{C} : 0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

$$\text{O} : u, \bar{u}, 0; \bar{u}, 0, u; 0, u, \bar{u}; \frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2}; \\ u+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}, \frac{1}{2}-u, u+\frac{1}{2}.$$

where for a unit cell $a_0 = 6.361 \text{ \AA}$, $\alpha = 46^{\circ}6'$ and $u = 0.243 \text{ \AA}$. It consists of planar CO_3 groups in which the carbon atoms are at the centers of equi-

(13) Wyckoff, Crystal Structures, vol II, Interscience

lateral triangles of oxygen atoms. The C-O distance is 1.25 A. The crystallography of calcite may also be described in terms of a hexagonal lattice in which the calcium and carbonate groups form alternating planes of atoms each perpendicular to the hexagonal c-axis. The structure of calcite is illustrated in figs. 1 and 2.

Pure calcite is transparent from the ultraviolet absorption edge which lies at approximately 210 m μ to the first infrared absorption band found at 1875 m μ . Those absorption bands which are located within the range of the Beckman instrument are shown in fig. 3. It was found that all these bands were anisotropic absorbing only light polarized perpendicular to the c-axis.

Optically calcite is highly birefringent with indices of refraction for the sodium D line of $\omega = 1.65849$ and $\epsilon = 1.48625$. At various wavelengths the indices of refraction⁽¹⁴⁾ are:

<u>Wave Length</u>	<u>Ordinary Ray</u>	<u>Extraordinary Ray</u>
198 m μ	-	1.578
340	1.701	1.506
589	1.658	1.486
760	1.650	1.483
1229	1.639	1.479

Calcite is found in nature colored yellow, red, violet and pale blue as well as colorless. It has been found⁽³⁾ that these colored forms can be bleached by heating, exhibiting thermoluminescence, and when exposed to radiation regain their colors. The chemical composition of yellow calcite

(14) Handbook of Chemistry and Physics 40th ed. page 2934 (1958-59)

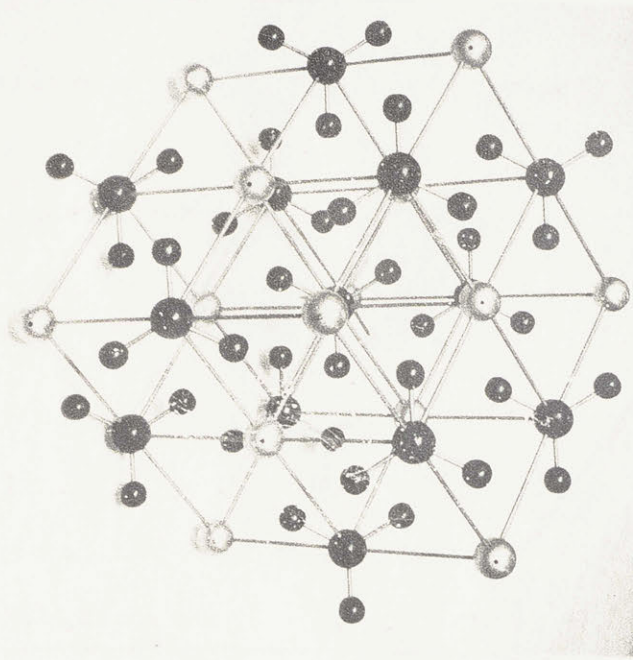
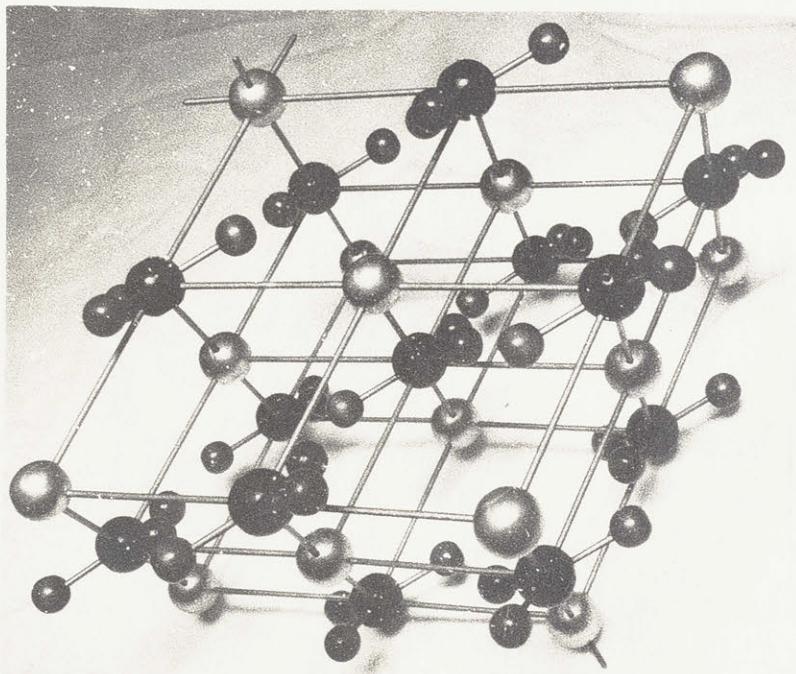


Figure showing Calcite structure.
c-axis shown pointing into page.

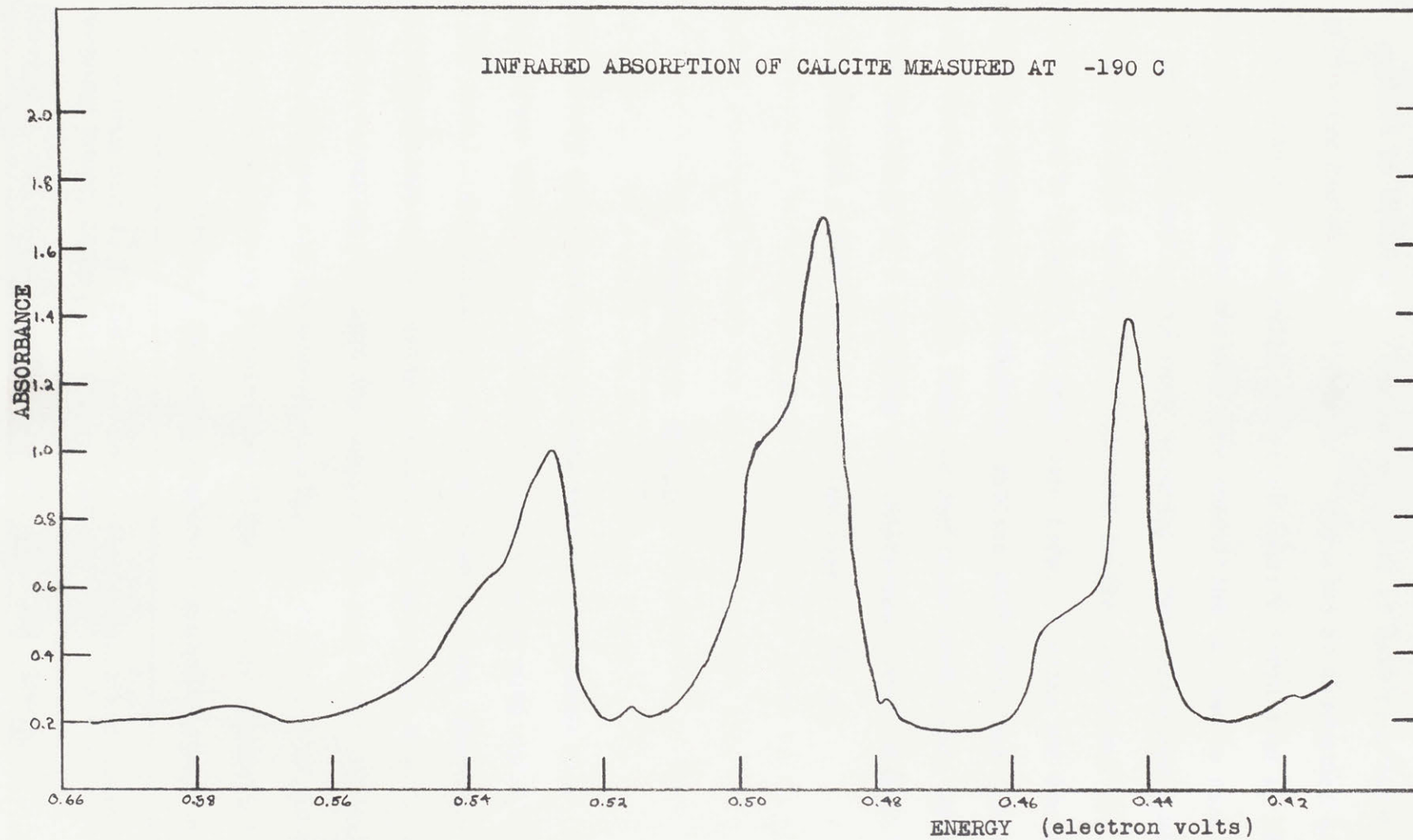
Fig. 1



View of Calcite structure showing parallel planes
of carbonate and calcium ions.

Fig. 2

Fig. 3



was determined by Headden⁽¹⁵⁾ who found traces of many rare earth ions as well as thorium and cesium. Przibram⁽¹⁵⁾ reported an absorption peak at 375 m μ in a sample of naturally colorless calcite irradiated by radium radiation. He questioned whether this coloration was due to rare earth ions or due to centers in the basic material. The absorption spectrum of pure colored calcite has not been reported in the literature.

Calcite can be obtained in very pure form. Clevins and Straumanis⁽¹⁶⁾ report finding samples of transparent calcite with less than 0.02% foreign material. The calcite samples selected for these experiments were highly perfect as indicated by a uniformly low absorption coefficient in the transparent portion and a very sharp absorption edge at 210 m μ .

EXPERIMENTAL RESULTS

Preliminary experiments on cleaved samples irradiated with electrons at 3 Mev showed that it is possible to color calcite with moderate dosages (10^4 - 10^5 rads). For comparison this was done at room temperature and at liquid nitrogen temperature using the cryostat described above. To prevent any possible bleaching by light the samples were irradiated in light tight chambers in this and all subsequent trials. The results obtained were essentially the same at both temperatures although better resolution was obtained at -190°C . Although the bands produced were quite stable at -190°C

(15) H. Przibram and J. E. Caffyn, "Irradiation Colours and Luminescence" Pergamon Press, London (1956), pg. 236-8.

(16) Clevins A. and M. Straumanis, Z. Phys. 116, 194 (1940).

there was some evidence of thermal bleaching during measurements made at room temperature. This will be discussed in greater detail later. As can be seen from fig. 4 there are at least two absorption bands present, one at 290 $m\mu$ (4.28 ev.) and the other at about 350 $m\mu$ (3.54 ev.).

To determine if any of the bands present were anisotropic, oriented calcite samples were prepared as described above. It was found that the band at 350 $m\mu$ was isotropic whereas the band at 290 $m\mu$ was anisotropic absorbing only when excited by light polarized perpendicular to the c-axis. This anisotropy can be seen in figs. 5 and 6. Identical absorption spectra were obtained for samples irradiated and measured at room temperature and at liquid nitrogen temperature.

To determine the effect of increasingly larger doses on coloration, an oriented sample of calcite was subjected to repeated irradiations. To prevent thermal bleaching between trials the temperature of the samples was kept at -190°C . The results are shown in figs. 5 and 6. It can be seen that no apparent shift of the absorption maxima for either band results from increasing the dosage. Also the half widths of the bands (isolated as explained in appendix 3) are approximately constant independent of dosage. This result is expected if the statistical behavior of the centers produced is constant independent of the total number present. From Smakula's formula⁽¹⁷⁾ it follows that the total number of centers present is proportional to the absorption coefficient of the band peaks.

The absorption peaks for the two bands are plotted in fig. 7. The coloration is rapid at first, then increases more slowly as saturation is approached.

(17) see appendix 3

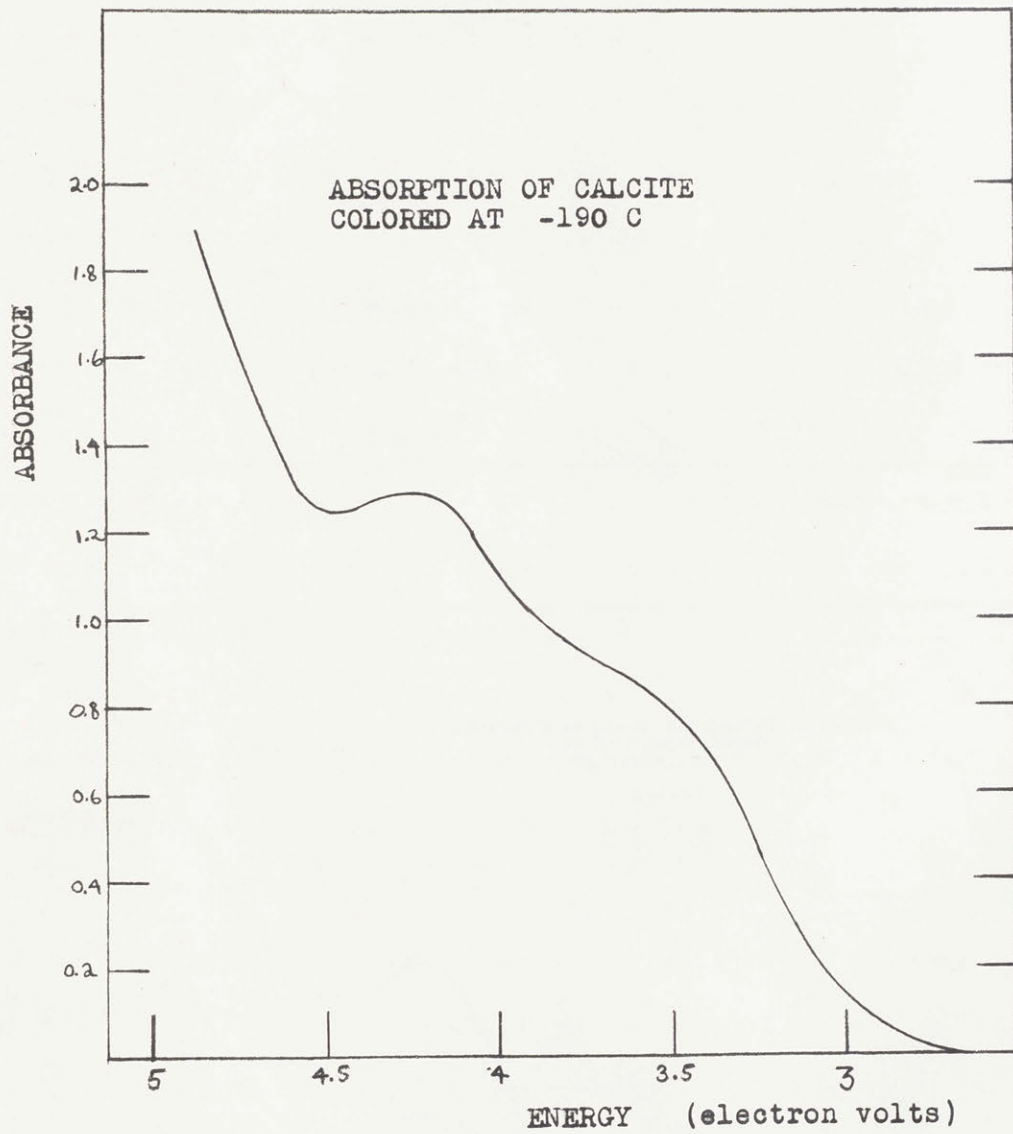


Fig. 4

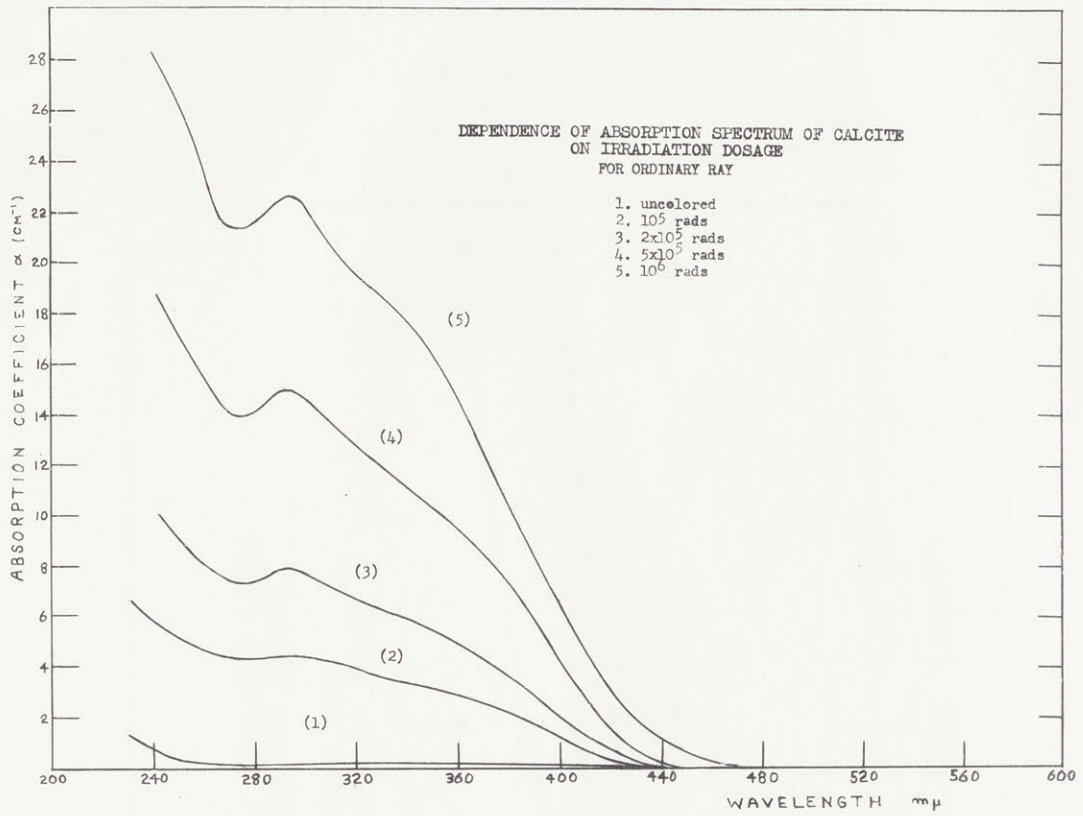


Fig. 5

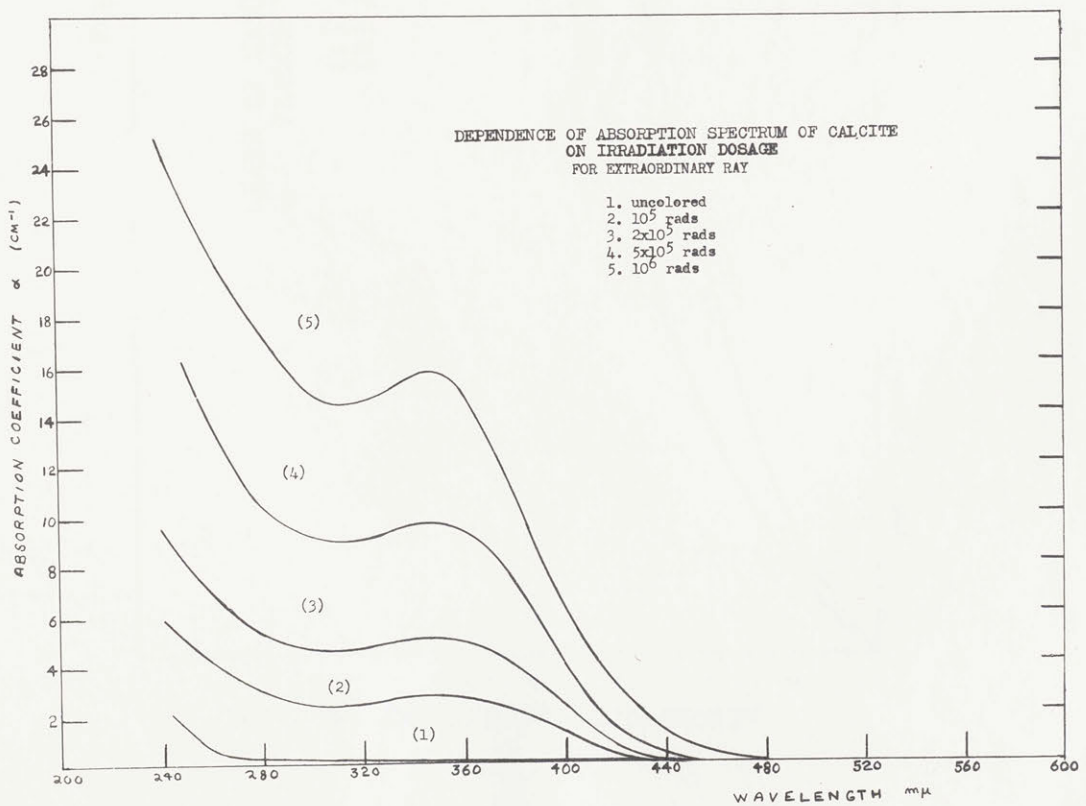
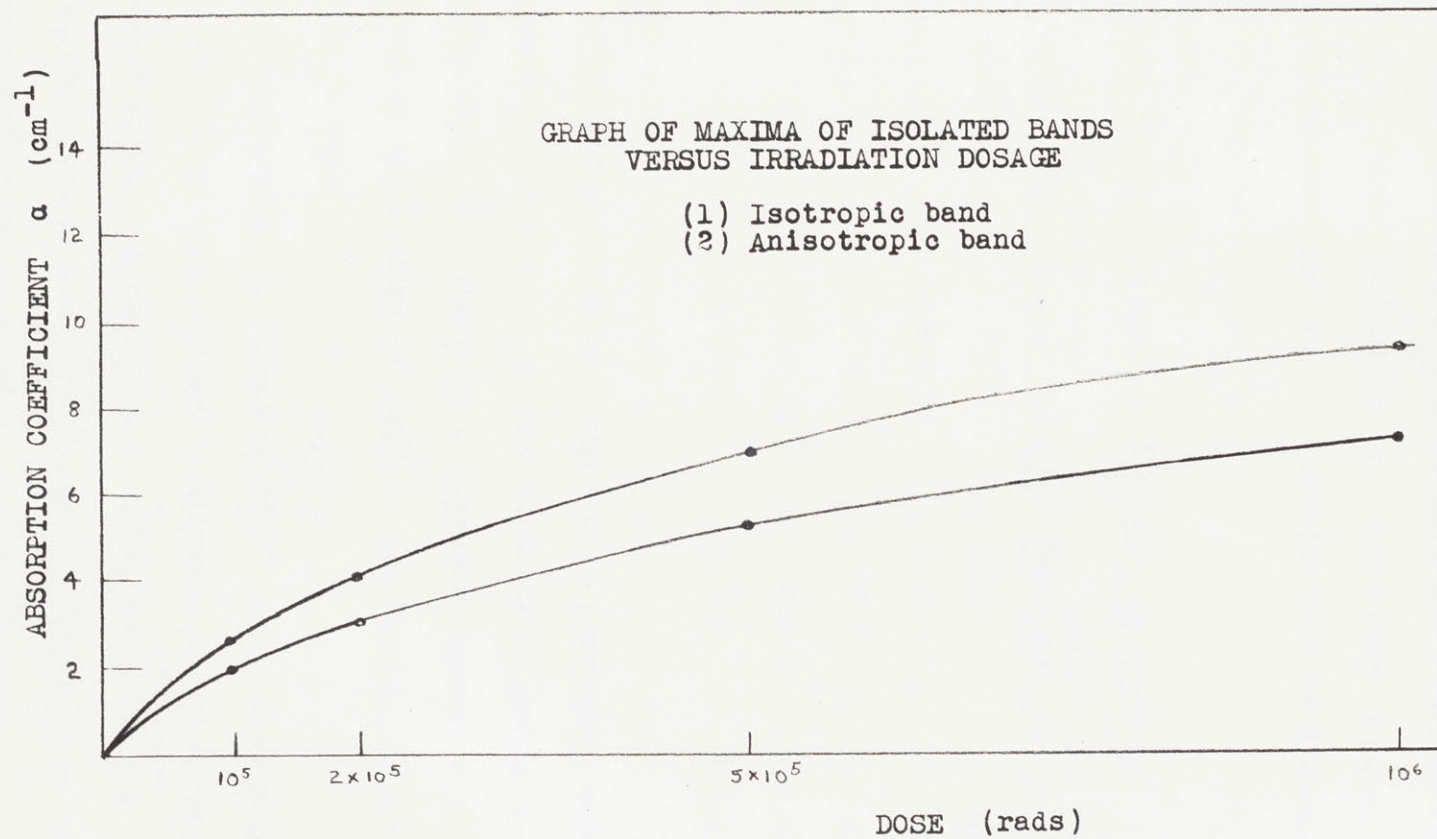


Fig. 6

Fig. 7



In these experiments complete saturation of the centers was not obtained.

Using Smakula's formula (see appendix 3) the approximate number of centers produced was computed. These results are tabulated below. Note that the number of centers associated with each band is equal at all intensities. Further implications of these results will be discussed later.

Number of Centers Produced by Electron Irradiation

Irradiation Dose	Isotropic Band		Anisotropic Band	
	Peak Max.	No. of Centers	Peak Max.	No. of Centers
(rads)	(cm^{-1})	($n_0 f$)	(cm^{-1})	($n_0 f$)
1×10^5	2.7	8.4×10^{15}	2.0	8.3×10^{16}
2×10^5	4.0	1.1×10^{16}	3.0	1.2×10^{16}
5×10^5	7.0	2.5×10^{16}	5.3	2.4×10^{16}
1×10^6	9.3	3.5×10^{16}	7.6	3.2×10^{16}

Preliminary experiments on recoloration of previously colored samples bleached by heating at 400°C for an hour (calcite is stable at temperatures up to 500°C) indicated that there is no permanent change in the defect structure caused by irradiation at least at low levels. However this should be investigated further.

In order to determine the effect of light on the absorption bands in calcite, colored samples were exposed to illumination at various wavelengths. Using the Beckman spectrophotometer as a light source (with a slit width of 1 mm) an irradiated crystal was exposed for an hour first to light at $290 \text{ m}\mu$ polarized perpendicular to the c-axis, and then to light at $350 \text{ m}\mu$ polarized parallel to the c-axis. Finally the sample was exposed for 20 minutes to

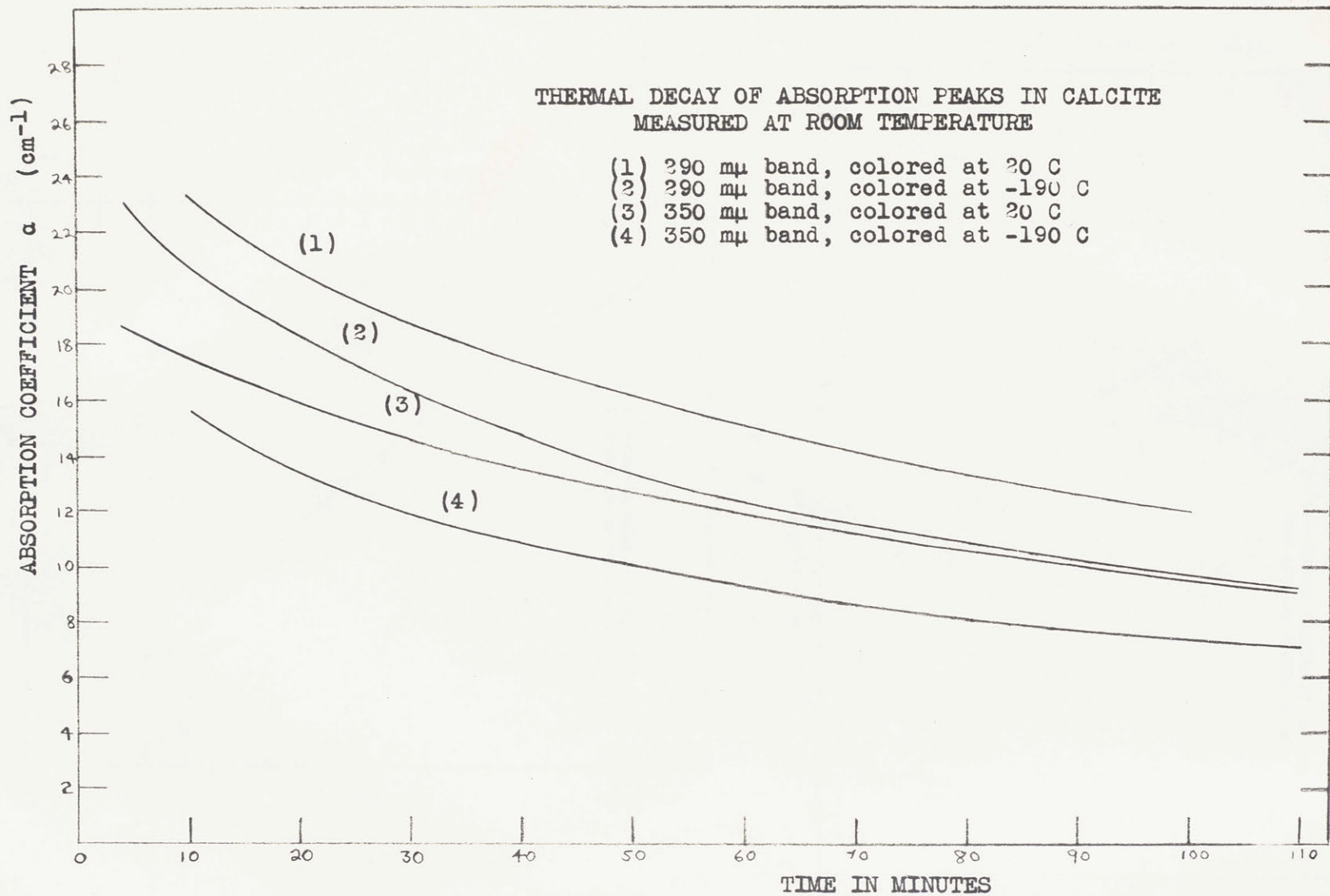
unpolarized light from an incandescent source (using ordinary glass). No noticeable bleaching effects resulted from any of these trials. Similar experiments are known to produce bleaching of color centers in most compounds.

Although the color centers are quite stable at -190°C they bleach readily at room temperature. A measurement of the absorption peaks at 290 and 360 $\text{m}\mu$ showed that (1) both bands bleach at almost the same rate and (2) coloration at room temperature and coloration at -190°C followed by room temperature bleaching result in identical bleaching rates. The results obtained are shown in fig. 8. It was found that weak bands identical to those described above were present in the calcite samples before irradiation. These bands are probably related to the previous history of the sample and may indicate that the centers are quite stable at low concentration.

Associated with the decay of the color centers is an orange luminescence which is quite intense immediately after irradiation and is still visible after eight hours. This luminescence was measured using a Cary model 11 spectrophotometer with a luminescence attachment. The luminescence band obtained as shown in fig. 9 had a peak at about 590 $\text{m}\mu$ (2.10 ev.). It can be seen that the band is assymetrical with greater intensity on the long wavelength side. The luminescence band was found to be isotropic.

In order to determine the decay rate of the luminescence a photocell and amplifier were used. Due to the limited sensitivity of this equipment it was possible to obtain data only for the first 120 minutes of the decay process. The results of these measurements plotted logarithmically are given in fig. 10. The decay appears to be approximately exponential in nature.

Fig. 8



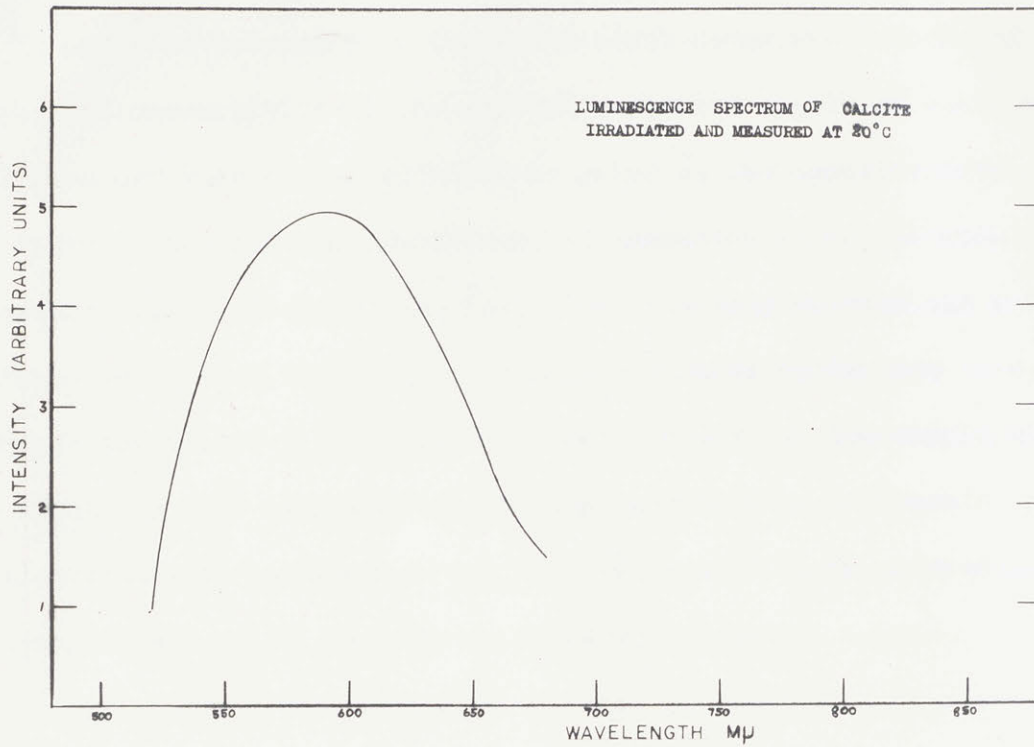


Fig. 9

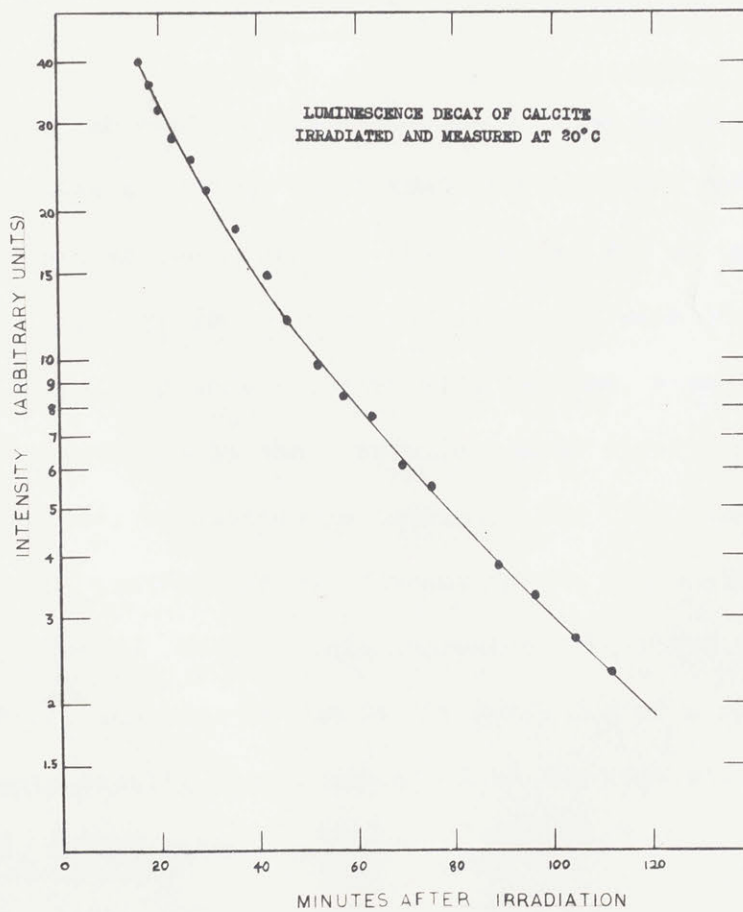


Fig. 10

In order to determine if the luminescent decay was associated with an increase of conductivity of the crystal a cleaved sample of calcite was irradiated and then coated with silver paint on two opposite faces. Wires were fastened to the silver coatings and connected in series with a 300 volt source and a sensitive ammeter. The resulting current was measured and found to be less than 5×10^{-12} amps. This is equivalent to a resistance greater than 6×10^{13} ohms or a resistivity for the sample greater than about 3×10^{14} ohms-cm. Apparently therefore no noticeable increase in conductivity is produced during the luminescent decay process. Hence electron migration, if present, is local in nature.

DISCUSSION

Two principal absorption bands have been found in calcite irradiated with electrons. One at 290 $m\mu$ is excited only by light vibrating perpendicular to the c-axis of the crystal; the other at 350 $m\mu$ is isotropic. This result suggests that the 290 $m\mu$ band is associated with the carbonate group and that the 350 $m\mu$ band is associated with calcium, since the former is intrinsically anisotropic in the crystallographic direction indicated above, and the calcium lattice position is intrinsically isotropic. It appears that an additional isotropic band adjacent to the fundamental absorption edge is also produced. Whether this increased absorption in the neighborhood of the absorption edge is due to the formation of a specific color center, or simply results from a breakdown of the edge structure due to crystal damage, is not known.

Several of the experimental results indicate a close connection between the two principal bands. As described above, calculations have shown that the number of centers associated with each of these bands is approximately equal at all coloration levels. Coloration of both bands proceeds linearly at first, then more slowly as saturation is approached. Thermal bleaching measurements show that both bands bleach at the same rate. On the other hand, optical bleaching studies have indicated that both bands are stable during moderate optical excitation.

As a possible mechanism to explain these results the following is proposed. CaCO_3 can be considered as an ionic crystal composed of Ca^{++} and CO_3^{--} ions. When the crystal is formed, the two extra Ca electrons are transferred to the CO_3 group forming an ionic bond. It is proposed that during irradiation some of these extra electrons are transferred back from the CO_3 groups to the Ca ions, thereby producing additional energy levels in both structures. It is these additional levels that produce the observed absorption bands.

It is doubtful that such a process would be stable at all even at -190°C if it took place in a perfectly regular lattice. Pekar⁽¹⁷⁾ asserts that excited states in a perfect crystal are always a result of excitation of the crystal as a whole and never result from an excitation in localized regions. Hence it is almost certain that the CO_3 electron is either transferred to a Ca ion through a defect in the lattice so that the two ions are effectively separated by a gap in the crystal, or that the extra electron is transferred to a calcium vacancy where it is trapped.

(17) S. I. Pekar "Untersuchungen über die Elektronentheorie der Kristalle" pg. 111, Akademie-Verlag, Berlin (1954)

In these cases the possible number of centers which can be produced is limited by the number of vacancies present. Although complete saturation was not obtained, experiments at high coloration indicate an approximate saturation density of about 5×10^{16} centers/cm³ for each band. The number of Ca ions in calcite is easily calculated and found to be 1.6×10^{22} ions/cm³. This is equivalent to a defect concentration of approximately $5 \times 10^{-4}\%$. This concentration is somewhat larger (by about a factor of 10) than that found in pure alkali halides, and probably results from additional defects produced by irradiation.

The average energy required to produce each center can easily be computed. It can readily be shown⁽¹⁸⁾ that for an irradiation dose of 1 rad at 3 Mev. the number of incident electrons is 1.5×10^8 per cm³ of material. Noting that each incoming electron has an energy of 3 Mev., the following energy values per center are obtained:

<u>Irradiation Dose</u> (rads)	<u>Number of Centers</u> (centers/cm ³)	<u>Average Energy Required per Center</u> (ev/center)
5×10^4	6.9×10^{15}	3.2×10^2
2×10^5	1.2×10^{16}	7.1×10^3
10^6	3.2×10^{16}	1.4×10^4

These calculations show that the efficiency of the color center production decreases rapidly as saturation is approached. At low levels of coloration, e.g. at 5×10^9 rads the energy value is about the same as that reported for color center formation in other substances⁽¹⁹⁾.

(18) see appendix I.

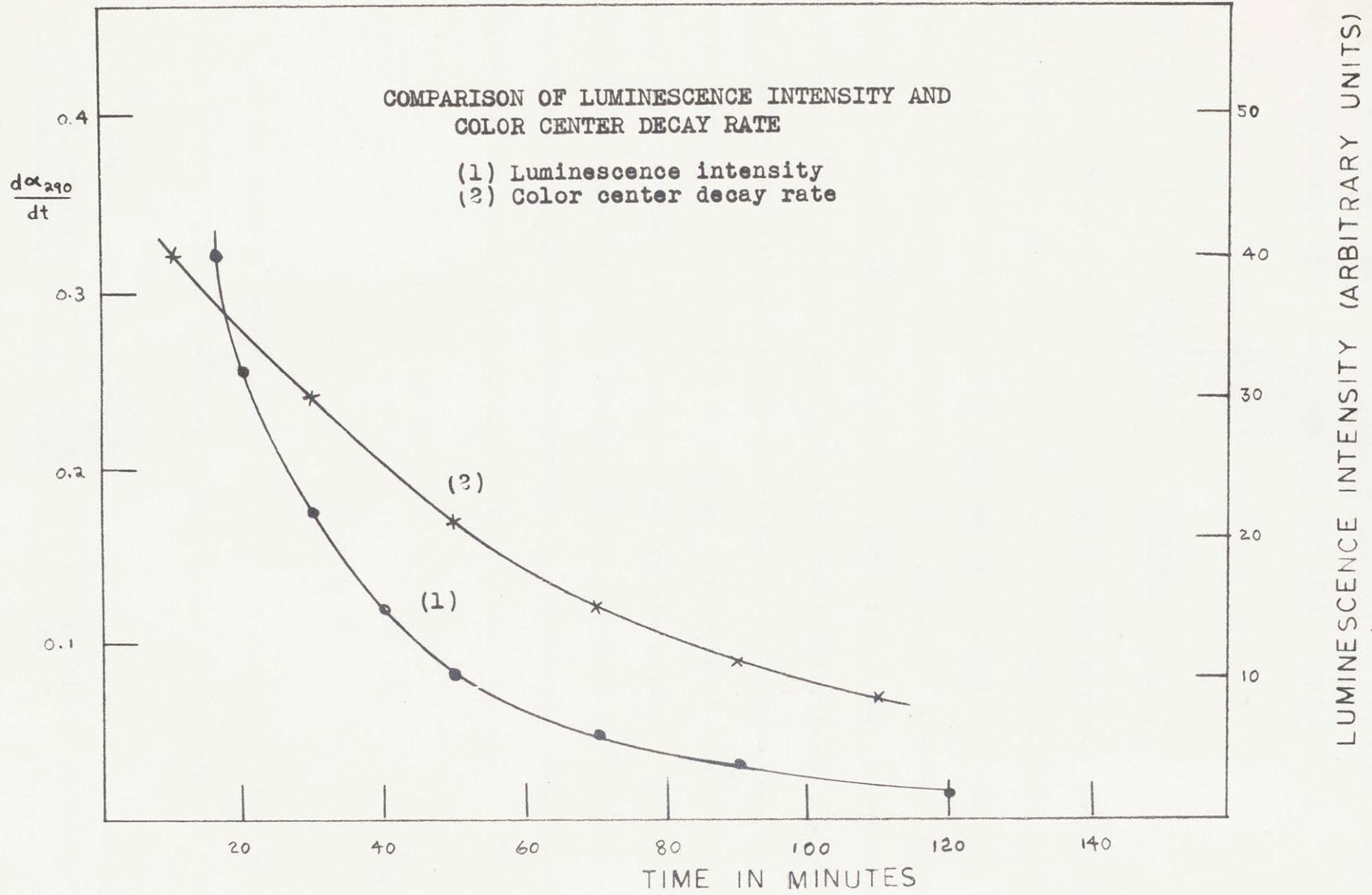
(19) see for example A. Smakula, Zeit. Physik, 138, 281, (1954)

At room temperature the absorption bands are unstable and decay thermally. According to the model proposed above, this should occur when electrons trapped at the Ca sites are thermally released and return to the CO_3 ions. Since this final configuration is more stable and hence has a lower energy than before, and since the direction of return of the electrons is random, an isotropic luminescence band should be produced. Such a band is actually observed at 590 μ .

If the luminescence is related to the destruction of Ca centers in a simple way its intensity should be proportional to the rate of change of the number of centers in this band. Using the experimentally observed fact that the half width of the band is constant at all levels of coloration it follows from Smakula's formula that the same proportionality should exist between time derivative of the absorption maximum for this band and the luminescence intensity. The results of such a comparison are plotted in fig. II. As can be seen from the graph, there is close agreement between the shapes of the two curves only after about 40 minutes of decay. At first the luminescence decays much more rapidly than the absorption band. This seems to indicate that the luminescence reaction is not as simple as might be thought. This aspect of the problem should be investigated further.

Finally the fact that the absorption spectrum is the same regardless of whether the crystal is colored at room temperature or at -190°C indicates that identical centers are produced at both temperatures. It should be noted however (see fig. 8) that slight differences in the thermal decay rates are found for the two cases, with coloration at -190°C producing an initially faster decay rate. This is probably due to the formation of a

Fig. 11



small proportion of weakly bound color centers at the low temperature. Similar results have often been reported for alkali halides⁽²⁰⁾.

APPENDIX I Effects of Electron Irradiation on Calcite

In order to displace an atom from its lattice position a certain amount of energy is required. Seitz⁽²¹⁾ estimated the magnitude of this energy E_d for interactions with fast particles as about $4 E_c$ where E_c is the energy of sublimation of atoms from the substance. For most compounds this energy is approximately $E_d = 25$ ev. Other researchers have placed this value as high as 40 ev. depending upon the orientation of the crystal lattice during irradiation. Using the value 25 ev. as the necessary displacement energy, it is possible to compute the incident energy of bombarding particles necessary to produce lattice transformations. With electrons a relativistic equation giving the energy transfer must be used. For heavier particles a non-relativistic equation is sufficient. The following equations are used for direct (forward) collisions.

$$E_m = 2E (E + 2 mc^2) / M_2 c^2$$

$$E_m = 4M_1 M_2 E / (M_1 + M_2)^2$$

where E_m is the maximum energy transferred by a moving particle of mass M_1 and energy E to a stationary atom of mass M_2 . m is the electronic mass and c is the velocity of light.

(21) see G. D. Dienes and G. H. Vineyard "Radiation Effects in Solids" Interscience Publishers New York (1957), pg. 56-58

(22)

One finds for various atomic weights of the stationary atoms the following energies:

atomic weight	<u>10</u>	<u>50</u>	<u>100</u>	<u>200</u>	
neutrons, protons	76	325	638	1263	(ev)
electrons, x-rays	0.10	0.41	0.68	1.10	(Mev)

This would indicate that in the case of calcite some lattice defects should be produced by electrons of the energy (3 Mev) used.

In order to determine the efficiency of the coloration process, it is advantageous to compute the number of electrons incident on a gram of calcite during irradiation. This can be done as follows. Since one rad is equal to 100 ergs/gram and 1 ev equals 1.6×10^{-12} ergs we have

$$1 \text{ erg} = \frac{10^{12}}{1.6} \text{ ev.} = \frac{10^6}{1.6} \text{ Mev.}$$

$$\text{Therefore } 1 \text{ rad} = \frac{10^8}{1.6} \text{ Mev./g.}$$

If d , the density equals the number of grams/cm³ we have for the total energy absorbed by one cubic centimeter of material upon exposure to 1 rad,

$$\frac{10^8}{1.6} d \frac{\text{Mev}}{\text{cm}^3} = NE$$

where N is the number of electrons absorbed/cm³ and E is the energy per electron.

$$\text{Therefore } N = \frac{10^8}{1.6E} d \frac{\text{Mev}}{\text{cm}^3},$$

or if E equals 3 Mev. and d equals 2.711 g/cm³,

(22) G. D. Dienes and G. H. Vineyard "Radiation Effects in Solids" Interscience Publishers New York (1957), pg. 56-58

$$\begin{aligned} N &= 5.65 \times 10^7 \text{ electrons/g/rad.} \\ &= 1.53 \times 10^8 \text{ electrons/cm}^3\text{/rad.} \end{aligned}$$

APPENDIX II Dosage and Range of Electrons in Calcite

Using aluminum as a typical absorber, Trump et al.⁽²³⁾ determined the relative ionization produced by a beam of 3 Mev. electrons at various points inside the material. The results of this experiment are shown in fig. 12. Although the data obtained in the experiment utilized an absorber of aluminum, it has been shown⁽²³⁾ that if the absorber thickness, r is expressed in terms of a new variable $R = r\rho$, where d is the density of the absorber, the results are valid for any material. This follows from the fact that the absorption of energy by the material through ionization is very nearly proportional to the density of material used.

Using these results one can calculate the approximate dosage administered to the sample in terms of the voltage and current used in the particle accelerator. The following formula is found to apply.

$$P = E I / \pi (D/2)^2 K_1 K_2 \text{ watts/g.}$$

where D is the diameter of a circular absorber, K_1 is the fraction of the total power absorbed in the range R and K_2 , approximately equal to 1, accounts for backscatter. In the above diagram K_1 is equal to the shaded area (where R is the thickness of the absorber) divided by the total area under the curve).

Using the results of this equation, irradiation time for any desired

(23) Trump, Wright and Clarke, J. Appl. Phys. 21, 345-48 (1950)

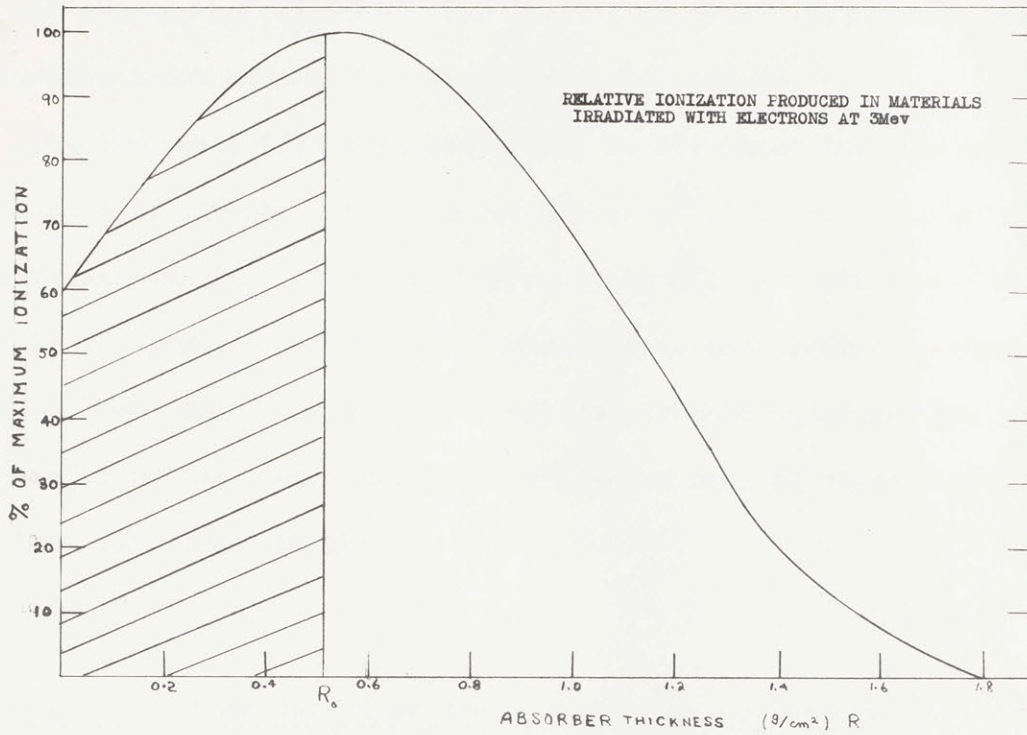


Fig. 12

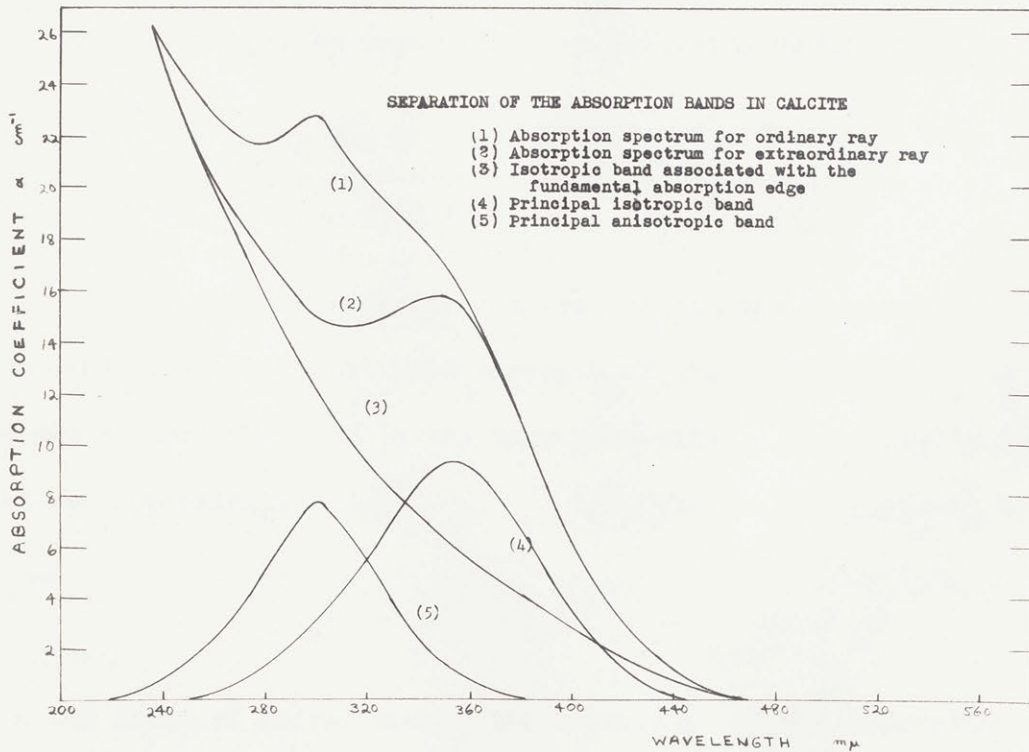


Fig. 13

dose can readily be computed. For the Van de Graaf instrument used these irradiation times were of the order of a few seconds.

From the above figure it can easily be seen that the penetration of electrons into the absorber is about 1.5 g/cm^2 at 3 Mev. For calcite having a density of 2.41 g/cm^3 this is equivalent to a thickness of 5.5 mm. Actually the greater part of the ionization is constrained to about 1.0 g/cm^2 or 3.7 mm, and for consistent results a sample thickness greater than this should not be used. Most of the samples used in these experiments were less than 3 mm thick.

APPENDIX III Computation of the Number of Color Centers

Using Smakula's formula⁽²⁴⁾ it is possible to compute the density of color centers present in a colored crystal if the absorption peak amplitude and the band width can be measured. The following equation is used:

$$n_0 f = \frac{9 k_m n_m \nu_F}{\pi (n + 2)^2 \epsilon^2} \frac{\Delta \nu_{1/2} (2\nu_F + \Delta \nu_{1/2})}{(\nu_F + \Delta \nu_{1/2})^2}$$

where n_0 is the density of color centers, ν_F is the frequency of the center of the band, f is the oscillator strength of the transition, k_m is the maximum absorption and $\nu_{1/2}$ is the band half-width. Using Beer's law and making the approximation that $\nu_F \gg \nu_{1/2}$, the following result is obtained.

$$n_0 f = 1.29 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_m W$$

with n the index of refraction of the material, α_m the absorption coefficient

(24) A. Smakula, Z. Phys. 59, 603 (1930)

and W the band width expressed in electron volts. In rough calculations such as given here f is usually considered to be unity.

To use this formula in the present situation it is necessary to separate the two principal absorption bands. This was done in all cases by first drawing in the approximate absorption produced by the additional band which is apparently centered near the fundamental absorption edge. This band was then subtracted from the absorption spectrum for the extraordinary ray to isolate the isotropic band. To isolate the anisotropic band the absorption spectrum for the extraordinary ray was subtracted from the absorption spectrum for the ordinary ray. The technique is illustrated in fig. 13 for a sample irradiated at -190°C with a dose of 10^6 rads.

Although this procedure is valid to a first approximation, it has several limitations. It assumes first of all that the anisotropic band is completely anisotropic, i.e. that it absorbs no light polarized parallel to the c -axis. That this is actually the case seems probable from fig. 13 since there is no evidence of a second peak for the extraordinary ray. More important, however, as described above, a third absorption band centered near the fundamental absorption edge of calcite is almost certainly present. At high levels of coloration, as in the case illustrated, the overlap of this band and the principal isotropic absorption band is considerable. Hence any errors in estimating the former will have a significant effect on the isotropic band. The results obtained for small irradiation dosages are more reliable since they do not suffer from this limitation.