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Color Centers in Calcium Fluoride Crystals

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by

A. Smakula

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Cambridge, Massachusetts

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September, 1954

COLOR CENTERS IN CALCIUM FLUORIDE CRYSTALS

by

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Abstract: Synthetic calcium fluoride crystals of various quality were colored by 2.5 Mev electrons, calcium vapor, and low energy electrons. Impurities and imperfections of the crystals were compared by ultraviolet transmission, density, ionic conductivity, and spectroanalysis. The best crystals show good transmission in the near and far ultraviolet, high density, low ionic conductivity, and have a low yield of color centers. Four absorption bands located at 2.16, 3.14, 3.70, and 5.50 ev are observed. The intensity ratio of the bands remains constant up to the highest coloration ($K = 3 \text{ mm}^{-1}$). Less perfect crystals show lower density, higher ionic conductivity and some absorption in the ultraviolet. The coloration is higher and the absorption bands vary somewhat in spectral position and intensity. It is concluded that the 4 bands observed in the best crystals are caused by electrons and/or holes trapped in lattice imperfections and not by chemical impurities as has been suggested by Lüty.

Introduction

Calcium fluoride can be colored like the alkali halide crystals, and exhibits several absorption bands in the visible and ultraviolet region. Natural CaF_2 crystals are colorless when pure, but usually are yellow, green, blue, or violet, because of chemical impurities or radioactive irradiation.¹⁾ The first

1) K. Przibram, "Verfärbung und Luminiszenz," Springer Verlag, Wien, 1953.

artificial coloration of natural CaF_2 was obtained by heating in a calcium melt.²⁾ The crystals were dark blue and could be bleached by heat at about 720°C in either an oxygen or hydrogen atmosphere. The crystals colored by this additive treatment contained an excess of Ca up to ca. 2.4 percent. No coloration was obtained in Na vapor.

A more extensive investigation was carried out by Mollwo³⁾ on natural crystals, colored by Ca vapor or electrons emitted from a pointed Pt cathode at temperatures between 400° and 1400°C . The colored crystals were gray and without selective absorption between 0.3 and $1.0\ \mu$ when cooled slowly to room temperature. Quenched, they exhibited two bands at 3.30 and at 2.35 ev called by Mollwo α and β . At an intermediate cooling rate, an absorption band near 2.15 ev appears. Mollwo concluded from conductivity and absorption shift with temperature that the α band corresponds to the F band in alkali halides. The nature of the β band, which appears always with the α band, remained obscure. The absorption at 2.15 ev was ascribed to colloids.

The coloration of natural crystals by radioactive radiation has been studied by Belar⁴⁾ and Eysank.⁵⁾ The coloration reached a saturation depending on the intensity of the radiation and on the particular crystal. In some crystals a strong local variation of the coloration was observed, indicating an inhomogeneous distribution of impurities. An absorption band at 2.0 ev shifts toward higher energy with prolonged coloration. After several months of irradiation with radium, the the crystals became brittle.

2) L. Wöhler and H. Kasarnowski, Z. anorg. Chemie 47, 353 (1905).

3) E. Mollwo, Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse 1, 79 (1934).

4) M. Belar, Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa 132, 45 (1923).

5) E. Eysank, Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa 145, 387 (1936).

Radium-colored crystals could be bleached by heat (up to 250°C) or by light at a rate depending on the nature of the crystal, the intensity of the coloration, and temperature. Crystals which color slowly, discolor slowly.

Herman and Silverman⁶⁾ found in some natural colored crystals three absorption bands at 2.13, 3.13, and 3.69 ev which could be bleached by heating the crystal to about 300°C for 72 hours. X-ray irradiation (150 kv for 6 h.) made the three bands reappear.

Coloration of synthetic CaF_2 crystals by hard X rays (200 kv) produced 4 absorption bands at 2.14, 3.09, 3.69, and 5.50 ev.⁷⁾ None of these lies in the same spectral region as the α or β bands of Mollwo. The rate of coloration decreases with exposure, but the intensity ratio of the 4 bands remains constant.

Thermal bleaching⁸⁾ of X-rayed synthetic CaF_2 at 100° , 180° , and 215°C affects all four bands equally, but the decay is not a simple exponential one. Analysing the bleaching-time curve, Barile⁸⁾ obtained three activation energies: 1.20, 1.26, and 1.38 ev. No bleaching by light was observed at room temperature and only little influence at higher temperatures. Later it was shown⁹⁾ that only the band at 2.14 ev is not bleached by light. The band at 3.09 ev bleaches easily, but a new band at 2.58 ev appears. Simultaneous exposure to light absorbed by the band at 2.14 and 3.09 ev bleaches both bands.

A striking difference between the alkali halides and calcium fluoride seemed to be that in the former identical absorption bands are produced by additive coloration or X rays. However, according to a recent investigation by Lüty¹⁰⁾ this difference disappears at a low degree of coloration: all four bands

6) R. Herman and S. Silverman, J. Opt. Soc. Am. 37, 871 (1947).

7) A. Smakula, Phys. Rev. 77, 408 (1950).

8) S. Barile, J. Chem. Phys. 20, 297 (1952).

9) A. Smakula, Phys. Rev. 91, 1570 (1953).

10) F. Lüty, Z. Physik 134, 596 (1953).

are formed by X rays or additive coloration. High additive coloring produces the 4 bands superimposed on a strong background absorption when the crystal is cooled down slowly: quenched crystals show only the α and β bands. Lüty concludes that the four bands produced at low coloration are caused by chemical impurities or defects, and that only the α and β band are characteristic of calcium fluoride crystals.

Hence, the nature of the color centers in calcium fluoride is still obscure. Two problems of particular interest are: 1) the nature of the impurities or imperfections which lead to the four absorption bands, and 2) the bleaching process by light. The present investigation deals with the first problem.

Crystals

The main objection to all previous investigations is the unknown quality of the material. It is known that CaF_2 crystals, natural or synthetic, contain varying quantities of impurities such as Mg, Sr, Cu, Fe, Si, K, and O.¹¹⁾ In the present study only synthetic crystals have been used. From crystals of Hargreaves* grown by Stockbarger method three types were selected (Nos. 1 - 3) which exhibit a strong difference in coloration. They were checked spectrographically for impurities of 70 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cb, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Ln, Mg, Mn, Mo, Na, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Ra, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Yb, Ty, Zn, Zr). Of these 70 elements not less than 20 were found in a distribution shown in Table 1.[†] Obviously, none of the samples is as pure as

11) D. C. Stockbarger, J. Opt. Soc. Am. 39, 731 (1949).

* Optovac, North Brookfield, Mass.

† The numerical values from 1 to 3 indicate an increase of impurity from traces (ca. $10^{-5}\%$ to the highest amount found which may be between 0.01 and 1%.

Table 1. Spectroanalysis of 3 types of CaF_2 crystals.

Element	Crystal			Element	Crystal		
	No. 1	No. 2	No. 3		No. 1	No. 2	No. 3
Ag	2	2	2	Mg	3	2	2
Al	3	1	2	Mn	2	1	1
B	1	-	-	Na	1	1	1
Ba	1	1	2	Pb	1	1	1
Cr	1	1	1	Si	3	2	1
Cu	1	1	1	Sn	1	1	1
Fe	3	2	2	Sr	3	3	3
K	3	-	1	Ti	2	-	-
La	1	-	-	V	1	1	1
				Yb	-	1	-

might be expected. Surprisingly, only traces of Pb are found in spite of the fact that it is used as scavenger (PbF_2) in the melt. Only a trace of Yb appears in Crystal No. 2; no other rare earth elements are found, which, according to Przibram, might be expected.

The spectrochemical analysis shows that Crystal No. 1 contains more impurities than Nos. 2 and 3, which are nearly alike. The rate of coloration increases, however, from Crystal No. 1 to 3. From the alkali halides it is known that the rate of coloration increases with impurities. If this rule applies also to CaF_2 , we must assume that cation impurities are not of primary importance. Oxygen is not detected by spectrographic analysis. It should be removed by the scavenger (PbF_2) in the melt, but how effectively, is not known.

The ultraviolet absorption of the three crystals before coloration is given

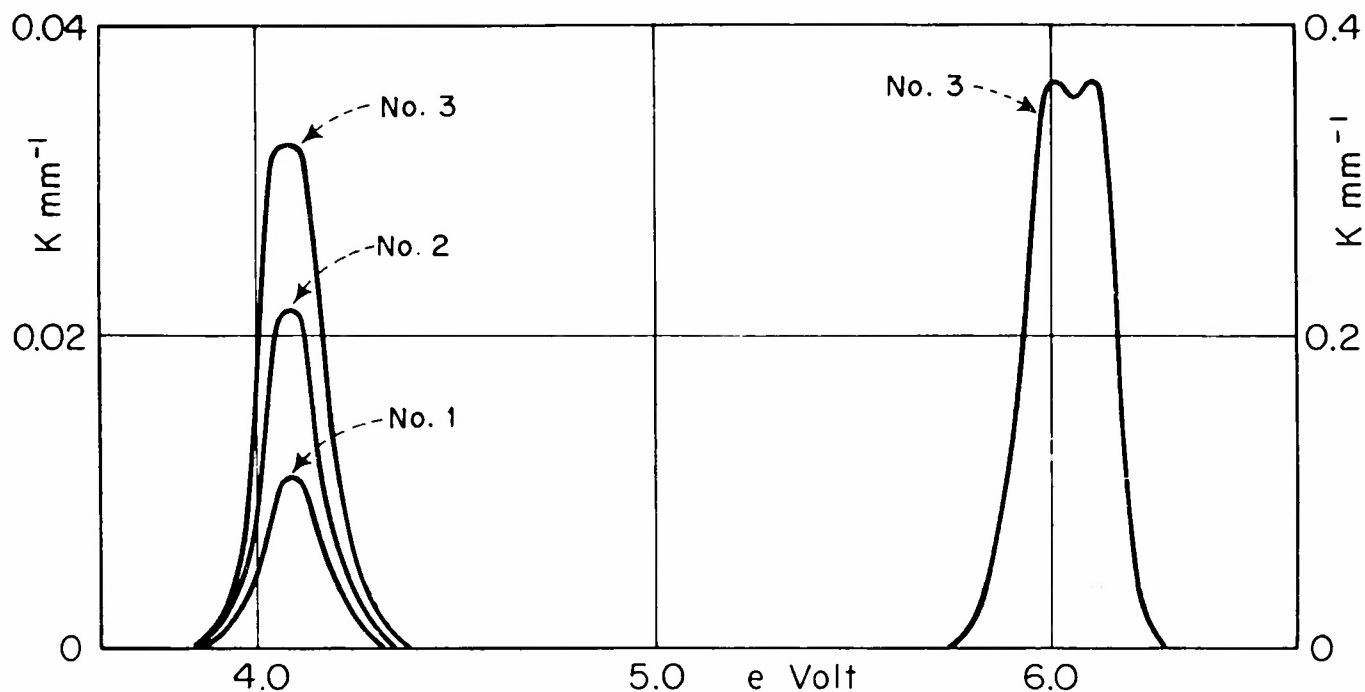


Fig. 1. Ultraviolet absorption of three CaF_2 crystals before coloration.

in Fig. 1.* All three crystals exhibit a very weak absorption at 3050Å (No. 1 the lowest). In addition, Crystal No. 3 has two stronger absorption bands at 2060 and 2030Å. In the vacuum ultraviolet below 1200Å Crystal No. 1 had an excellent transmission; the transmission of the other two crystals in this region is unknown.

Crystal No. 1 showed the highest density (flotation method), that is, the lowest amount of vacancies. This is confirmed by its low ionic conductivity in the temperature range from 100° to 200°C (Fig. 2). In BaF_2 , the ionic conductivity is carried by F ions only. If we assume that CaF_2 is similarly an anionic conductor, the higher ionic conductivity of Crystals 2 and 3 points to

* The absorption measurements were made with a Cary Recording spectrophotometer using a quartz double-monochromator between 2000 to 8000Å.

a higher amount of negative ion vacancies. A simple exponential representation ($\sigma = \sigma_0 e^{-\epsilon/kT}$) leads to an activation energy $\epsilon = 0.81$ ev.

Coloration by Electrons of High Energy

This type of coloration involves two effects: the penetration of primary electrons and the production of secondary electrons. For each electron introduced into the crystal, a negative ion

(F^-) has to disappear in order to preserve electric neutrality. Thus, the primary electrons create negative ion vacancies, but their number is small and this effect here is negligible. The secondary electrons ejected from negative ions leave positive holes behind and migrate until they are trapped by impurities and negative-ion vacancies, or recombine with positive holes.

Electrons of 2.5 Mev were chosen for this coloration for two reasons: the exposure time is short (up to few minutes) and the coloration can be carried out at room temperature. Thus no strain is introduced as in the case of additive coloring and subsequent quenching. The specific radiation dose of electrons was varied between 10^5 and 10^7 roentgens. The crystal samples were at least 5 mm thick while the penetration depth of electrons was only 3 mm. The heat developed by absorbed electrons is 2 cal/gm for 10^6 roentgens. To avoid a

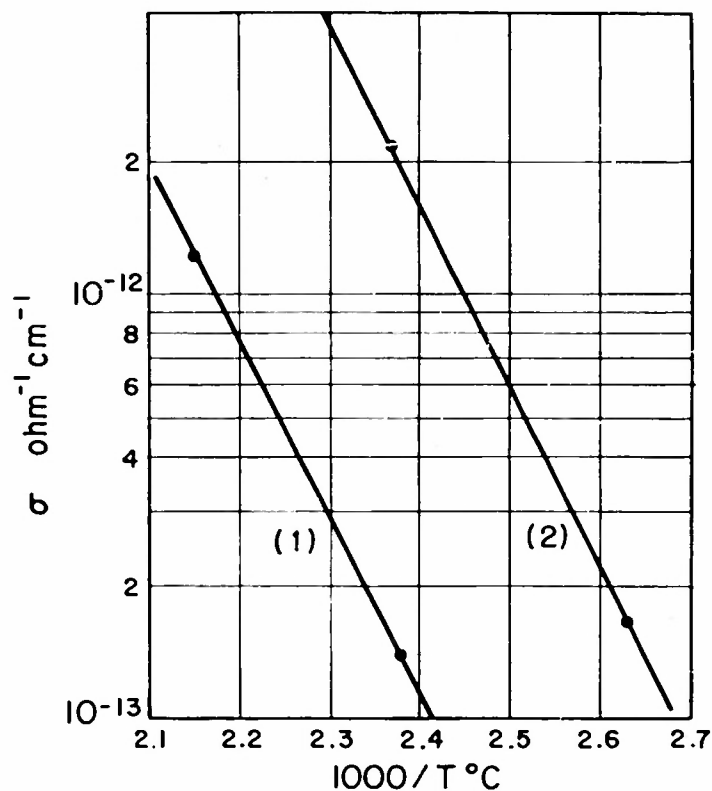


Fig. 2. Ionic conductivity of CaF_2
Crystals Nos. 1 and 2.

warming up, the crystals were immersed in ice water during exposure, and at doses above 10^6 roentgens the radiation was applied intermittently with intervals of several minutes.

The absorption curves obtained at room and liquid-nitrogen temperature, are shown in Figs. 3 to 8; the spectral position of the bands is summarized in Table 2. Their number, position, and intensity varies with the crystal type.

Table 2. Absorption bands in ev of three CaF_2 crystals colored by 2.5 Mev electrons (10^6 roentgens), measured at room and at liquid-nitrogen temperature.

Crystal no.	Temperature	Electron volts							
1	room	-	-	2.16	-	3.14	3.70	-	5.50
	liquid N_2	-	-	2.12	-	3.17	3.72	-	5.55
2	room	-	1.65	2.06	2.38	3.24	3.75	4.75	-
	liquid N_2	1.55	1.66	2.03	2.43	3.26	3.78	4.80	-
3	room	-	-	2.06	2.50	3.23	3.81	-	-
	liquid N_2	-	-	2.02	2.51	3.25	3.84	-	5.15

Three absorption bands, located at 2.06 to 2.16 ev; 3.14 to 3.24 ev; and 3.70 to 3.81 ev, seem to be common to all 3 crystals. The first band is at the shortest wavelength in Crystal No. 1, while the other two at the longest wavelengths as compared with the two other crystals. At low temperatures band I shifts toward longer, while bands II and III shift toward shorter wavelengths. Only in Crystal No. 1 does the intensity ratio of all 4 absorption bands remain constant up to the densest coloration ($K = 3 \text{ mm}^{-1}$); the coloration for this crystal is the lowest.

Although the other crystals were colored up to $K_{\text{max}} = 4.5 \text{ mm}^{-1}$, no absorption bands could be obtained which correspond exactly to Mollwo's a and

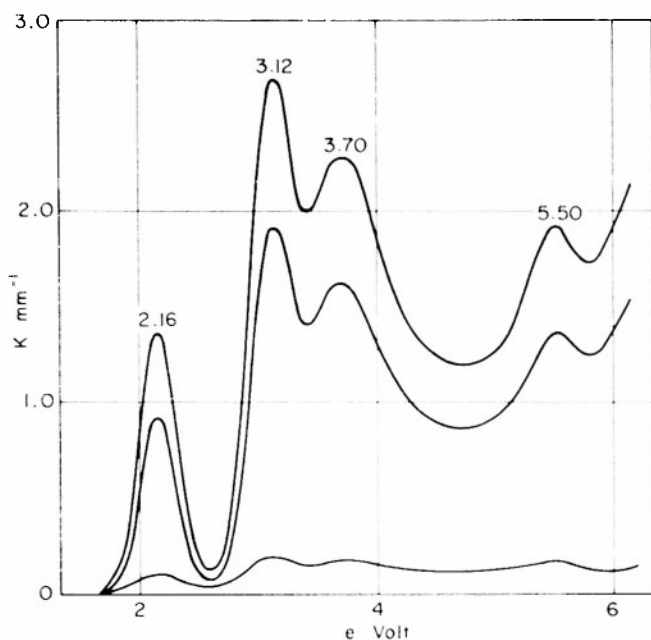


Fig. 3. Absorption of colored CaF_2 Crystal No. 1 at room temperature.

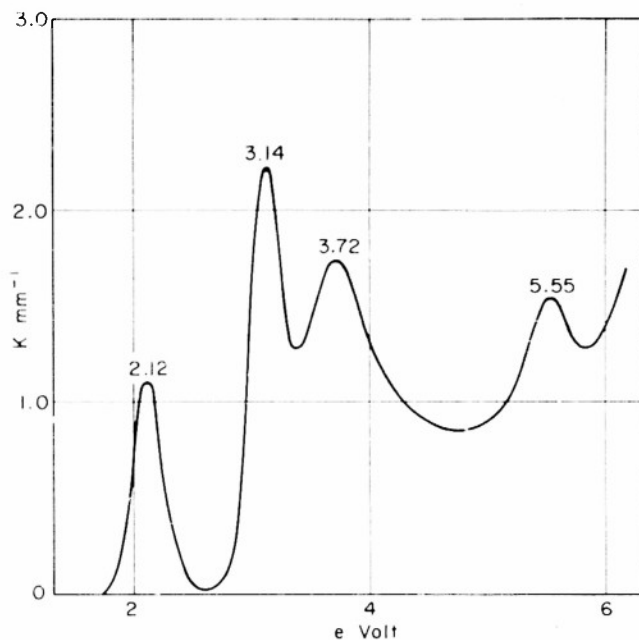


Fig. 4. Absorption of colored CaF_2 Crystal No. 1 at liquid N_2 temperature.

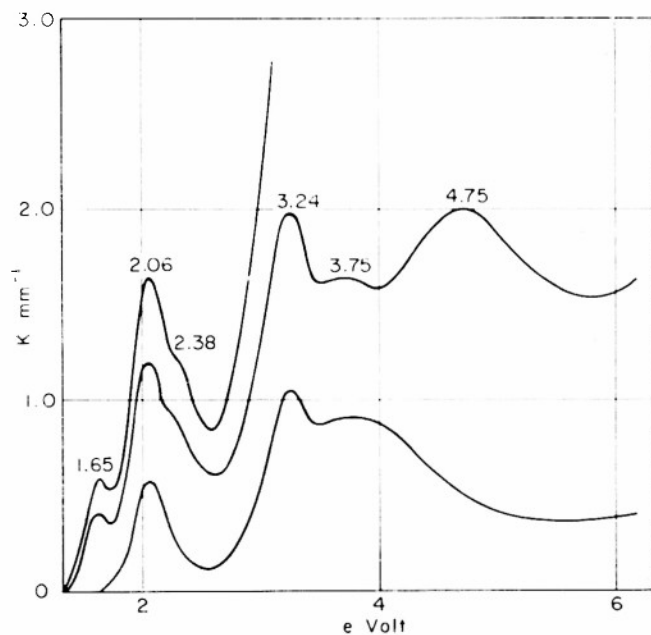


Fig. 5. Absorption of colored CaF_2 Crystal No. 2 at room temperature.

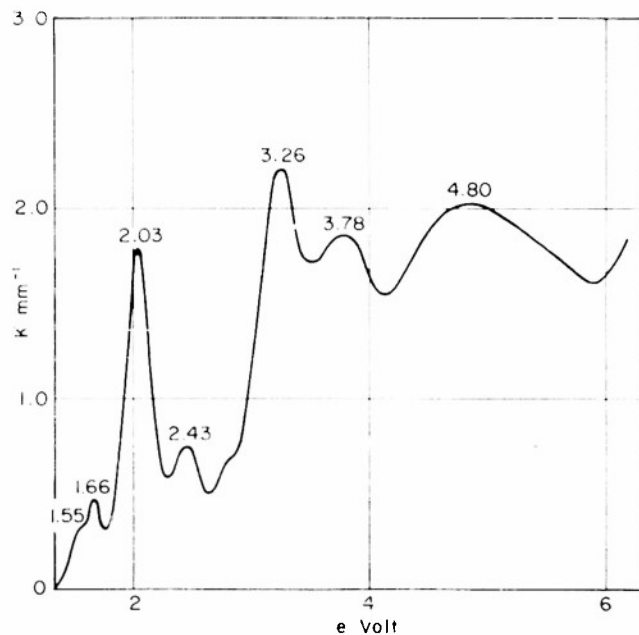


Fig. 6. Absorption of colored CaF_2 Crystal No. 2 at liquid N_2 temperature.

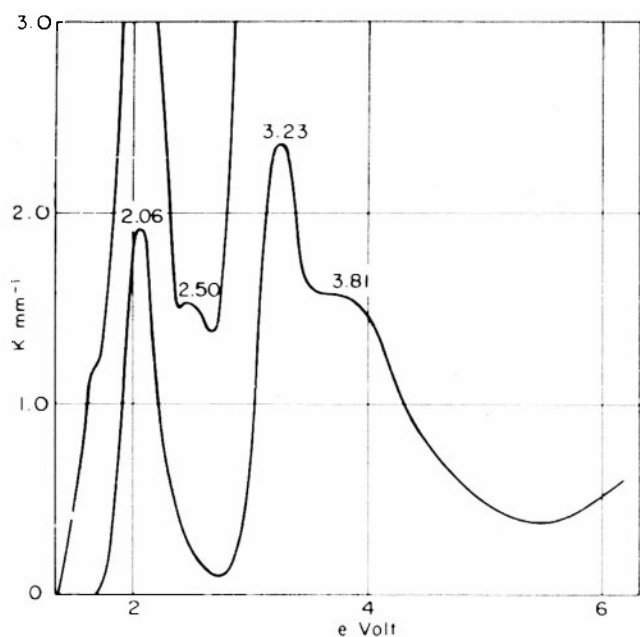


Fig. 7. Absorption of colored CaF_2 Crystal No. 3 at room temperature.

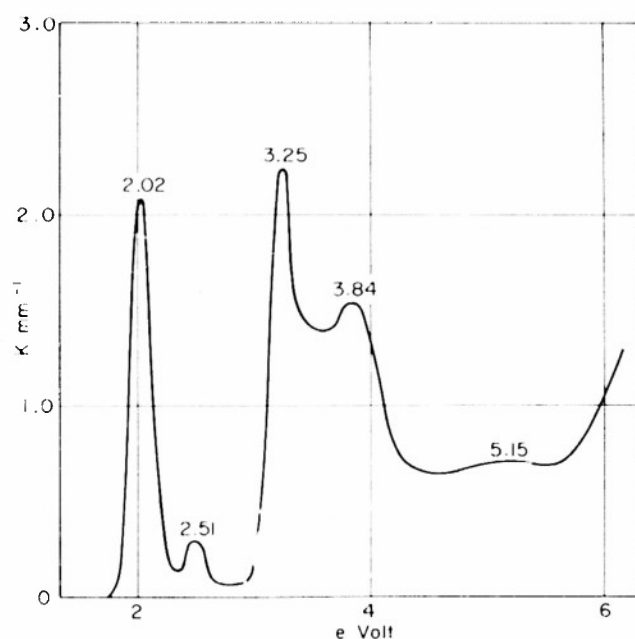


Fig. 8. Absorption of colored CaF_2 Crystal No. 3 at liquid N_2 temperature.

β bands.

Yield of Electron Coloration

To calculate the yield of coloration one needs to know the electron energy transferred and the number of color centers produced. The electron energy is computed from the radiation dose in roentgens ($1 \text{ r} = 83 \text{ ergs/gm}$). The number of color centers is determined from the height and half width of the absorption bands¹²⁾ as

$$N = 1.31 \times 10^{17} \frac{n}{(n^2 + 2)^2} KH,$$

where n is the refractive index of the crystal at K_{max} , K the absorption coefficient in cm^{-1} , and H , the half width of the band in eV. This equation assumes that the Lorentz factor is $4\pi/3$, the oscillator strength unity, and H small compared with oscillator frequency. For the band at ca. 3.0 eV and initial coloration, the

¹²⁾ A. Smakula, Z. Physik 59, 603 (1930).

yield for the three crystal types is given in Table 3. It increases from Crystal No. 1 to No. 3, and decreases with increasing coloration because of recombination. Although absorption coefficients over 4 mm^{-1} have been obtained, a saturation could not be reached.

Table 3. Yield of coloration for three CaF_2 crystals.

	No. 1	No. 2	No. 3
Concentration of color centers per cm^3	1.8×10^{16}	6.0×10^{16}	13×10^{16}
Yield color centers per evolt	3.7×10^{-4}	1.2×10^{-3}	2.7×10^{-3}

Thermal Bleaching

Since the three types of CaF_2 crystals showed a strong difference in coloration, also differences in bleaching were expected. Visual observation proved that crystals that color stronger bleach faster. To check whether all bands bleach simultaneously, the absorption was determined immediately after coloration and four days later. The change of absorption (Fig. 9) shows that all bands bleach simultaneously except for absorption above 5 ev in Crystals Nos. 2 and 3. The bleaching in all three crystals and for all three bands is proportional to the primary intensity of the bands (Fig. 10).

Bleaching, as a function of time, is not a single decay process, as already stated by Barile.⁸⁾ Similarly to the alkali halides, here also "soft" and "hard" centers may be distinguished or a transition from very unstable centers to stable ones. Generally, the color centers in CaF_2 are much more stable than those of the alkali halides, but coloration at lower temperatures produces centers that

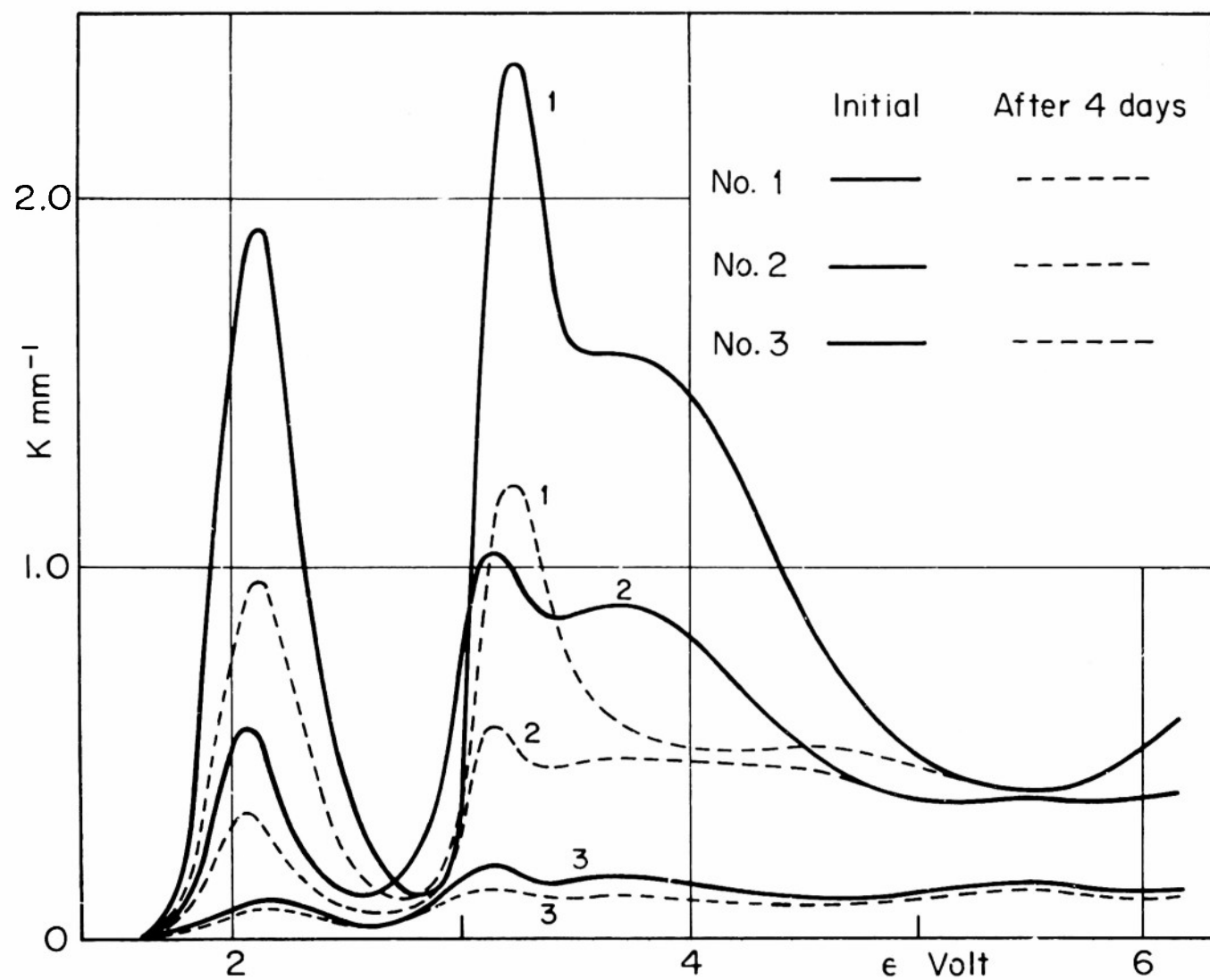


Fig. 9. Thermal bleaching of CaF_2 crystals colored by 3×10^5 Mev electrons.

are very unstable at room temperature.

Bleaching at higher temperature differs in Crystal No. 1 from that in Nos. 2 and 3. In Crystal No. 1 the bleaching at 100°C is similar to that at room temperature, only the rate is higher; all bands decrease proportionally

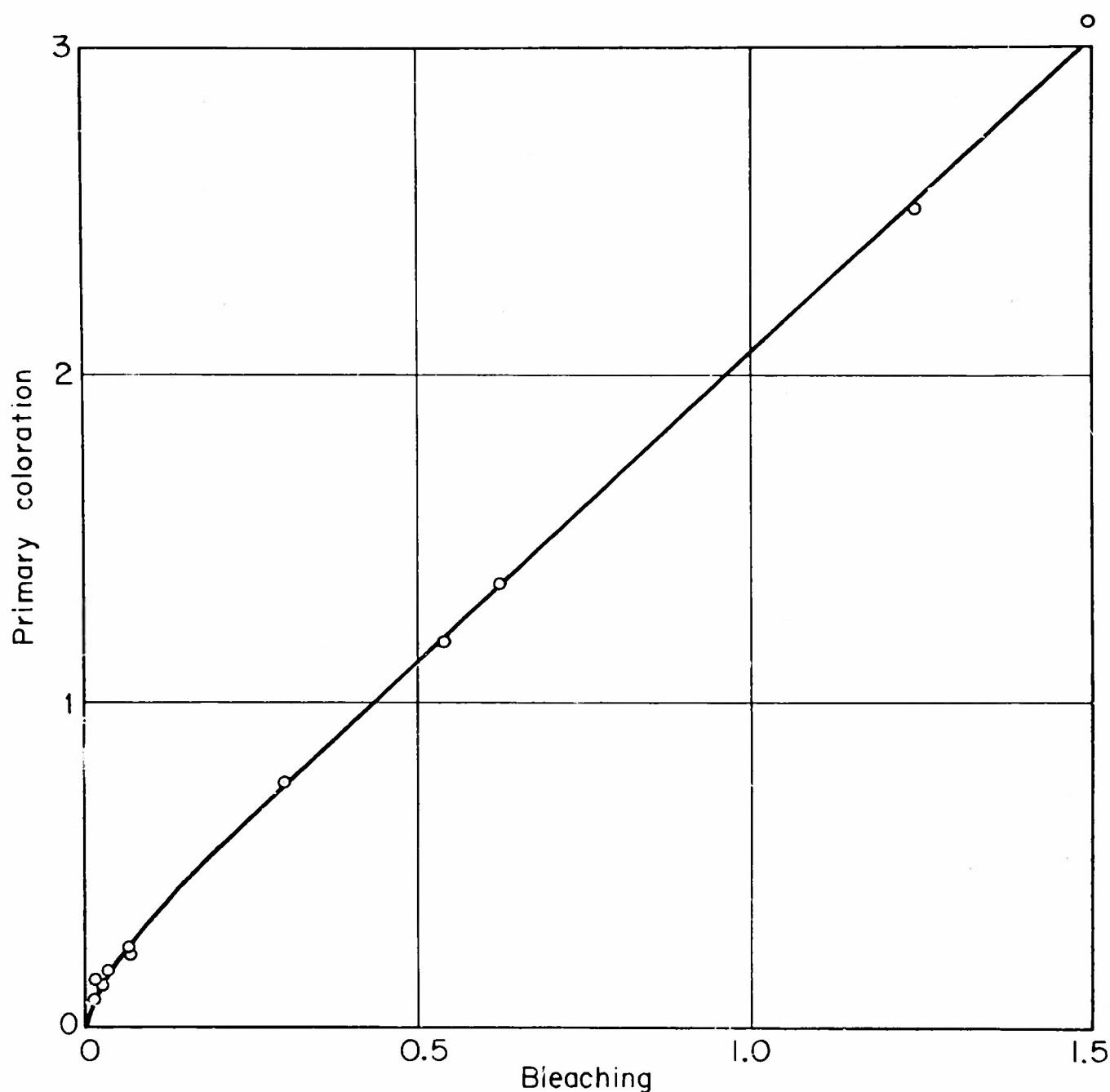


Fig. 10. Decrease of coloration vs. the primary intensity of coloration.

to their intensities. In the other two types the bleaching at 100°C changes the absorption spectrum strongly (Figs. 11 and 12). Before bleaching there are three bands, after bleaching up to 15 bands. The appearance of a great number of

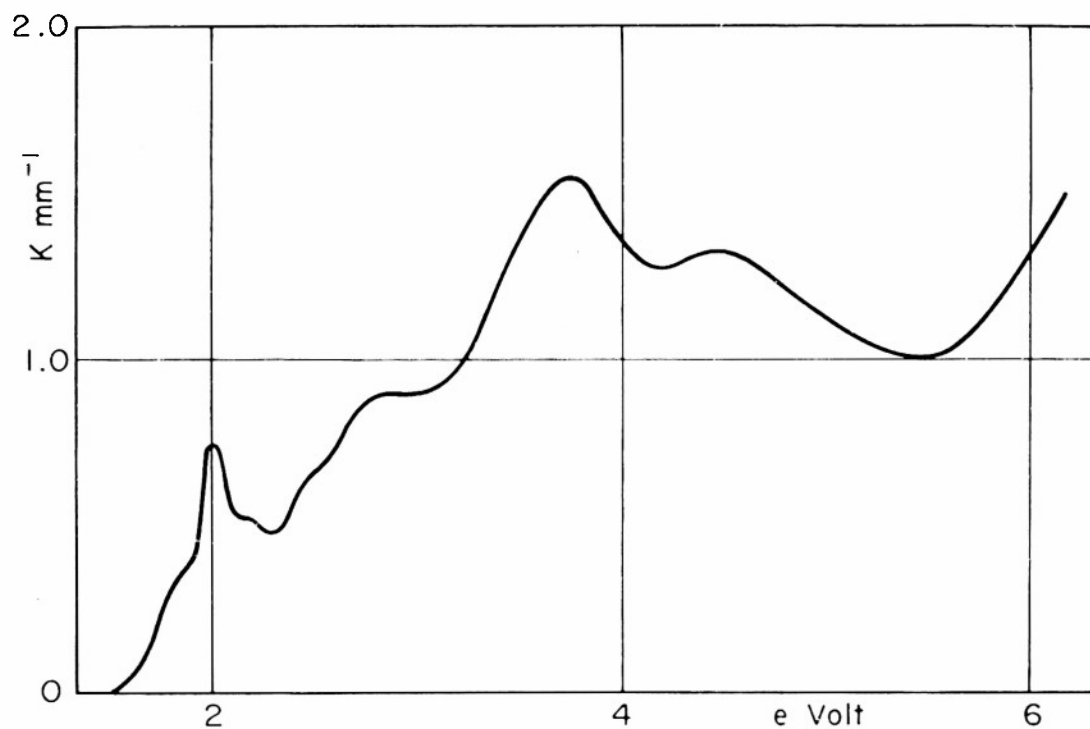


Fig. 11. Bleaching of CaF_2 Crystal No. 2 at 100°C measured at room temperature.

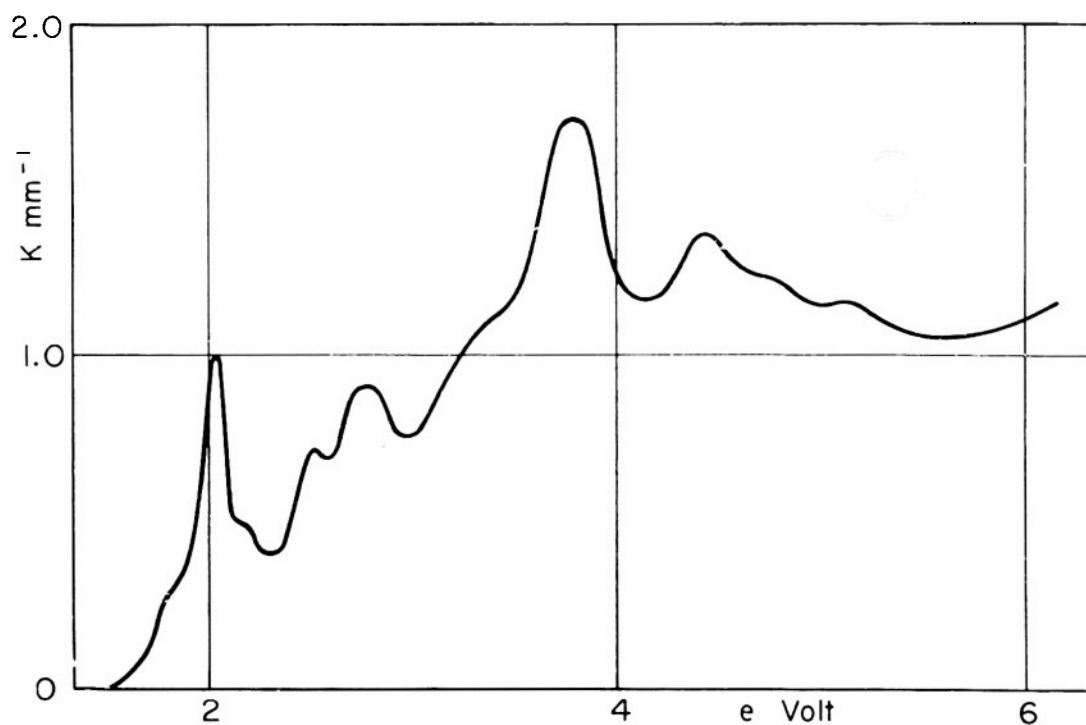


Fig. 12. Bleaching of CaF_2 Crystal No. 2 at 100°C measured at liquid N_2 temperature.

new bands in Crystals Nos. 2 and 3 indicates the variety of electron traps in these crystals.

Additive Coloration

Since it was impossible to obtain the α and β bands by coloration with electrons of high energy, samples were colored by Ca vapor. This additive coloration was carried out in evacuated Vycor tubes between 650° and 800°C . After coloration the glass tubes were immersed in water and crushed immediately after cooling. One hour of additive coloration at 650°C produced in Crystal No. 1 the absorption bands produced by high-energy electrons. The absorption of Crystal No. 2, colored in a simultaneous experiment, is completely different (Fig. 13), but the same as when colored by electrons. Additive coloration at 700°C leaves the band system in Crystal No. 1 the same; in Crystal No. 2 the bands at longer wavelength become broader. Crystal No. 1 appears blueish, No. 2 reddish. When the crystals colored at 700°C were dropped directly into water they became hazy, very brittle and not further useful for absorption measurements.

Coloration by Electrolysis

Coloration, using a pointed Pt cathode at 800°C , led to the same results as additive coloration. (The formation of dendrites was minimized by using a cathode edge instead of a point.) After very strong and prolonged coloration, the crystal surface was covered with white spots which gave an alkaline reaction; the crystal was partially hydrolysed. It is known that CaF_2 hydrolyses at temperatures even much lower (down to 100°C ¹³). Thus a coloration at high temperatures in the open air leads to chemical decomposition.

13) D. C. Stockbarger, Office of Scientific Research and Development, Report No. 4690, 1944, p. 34.

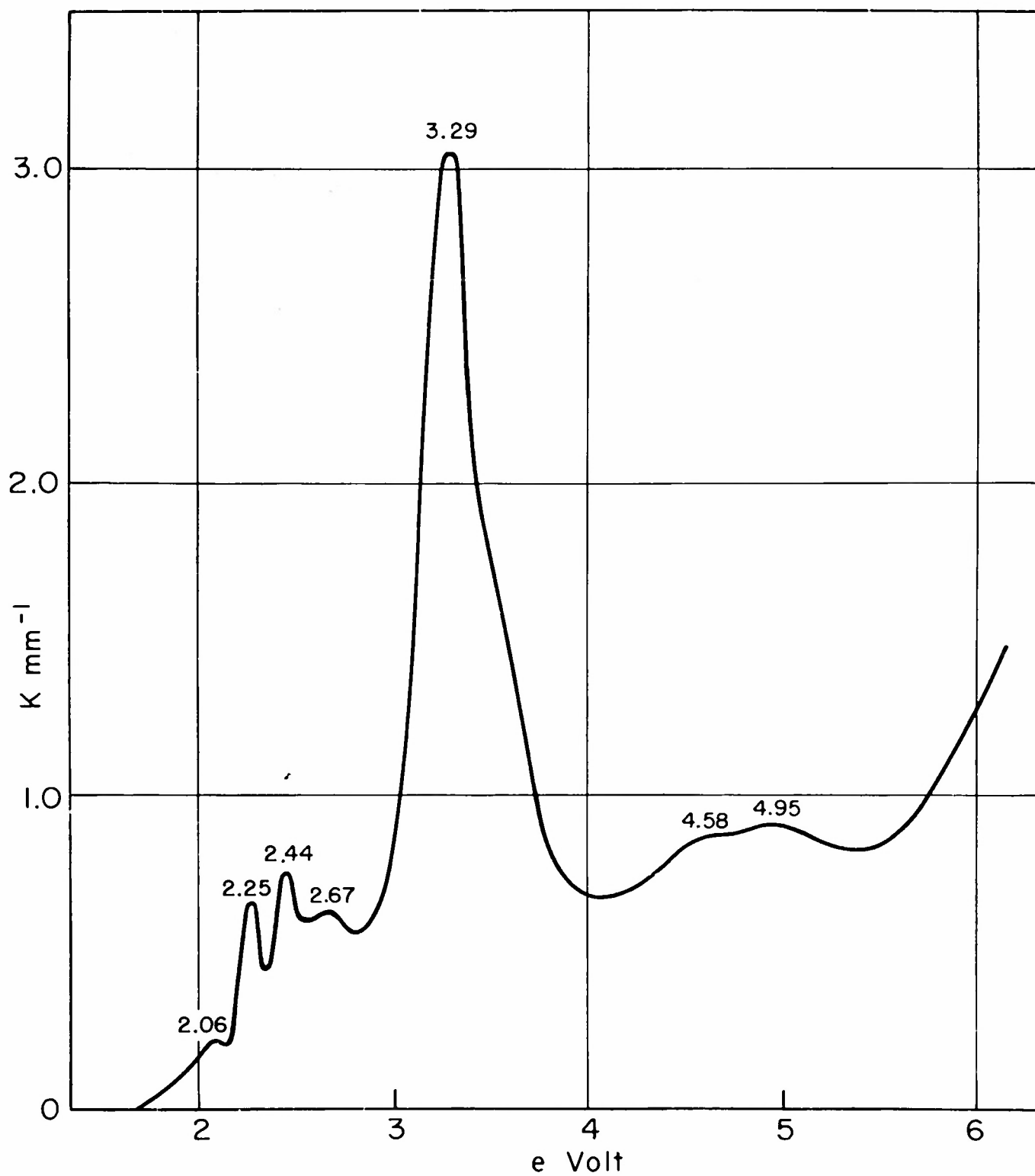


Fig. 13. Absorption of additively colored CaF₂ Crystal No. 2.

Discussion

Table 1 shows that even the best synthetic CaF_2 crystals contain a great variety of impurities. These cationic impurities, however, seem to be not directly or only to a slight degree connected with the formation of color centers. The main impurity of strong influence on color centers seems to be oxygen which, as demonstrated by Stockbarger, is a principal obstacle in growing CaF_2 crystals. The presence of oxygen in CaF_2 crystal produces negative ion vacancies which cause a decrease of density and an increase of ionic conductivity and of coloration. Crystals with high density, low conductivity, and good transmission in the near and far ultraviolet give weak coloration. The best crystals colored either by X rays, electrons, or metal vapor exhibit a system of four bands of approximately the same spectral position (Table 4) and of constant intensity ratio. Since the band system of Crystal No. 1 is most stable and simple in coloration and bleaching, it is assumed that it is not directly connected with impurities but belongs essentially to the CaF_2 lattice vacancies. Only the first two of these bands can be explained as an excitation and ionization transition. The nature of the other two is still obscure. Only at very strong coloration from a Pt cathode, where a high absorption background is produced, the band system changes and only the two bands at 2.17 and 3.17 eV remain; their intensity ratio is changed from 1:2 to ca. 1:1. This change is probably caused by oxygen contamination (possibly hydrolysis) at high temperature during the coloration process.

Crystals of lower density and higher ionic conductivity exhibit a higher coloration rate and a change of the bands in spectral position and intensity. During prolonged coloration new absorption bands appear and the intensity ratio does not remain constant. The thermal bleaching is higher and leads to the formation of new bands.

Table 4. Absorption bands of CaF_2 crystals colored by high-energy electrons, Ca vapor and pointed cathode.

Crystal no.	Coloration by	Electron volts							
1	Electrons	-	2.15	-	-	3.14	3.70	-	5.50
	Ca vapor	-	2.17	-	-	3.17	3.67	-	5.50
	Point cathode	-	2.17	-	-	3.17	-	-	-
2	Electrons	1.65	2.06	2.25	2.38	3.24	3.69	4.67	-
	Ca vapor	-	2.06	2.25	2.44	3.29	-	4.58 4.95	-
	Point cathode	-	-	2.25	2.41	3.25	3.67	-	5.50
3	Electrons	1.67	2.06	-	2.52	3.23	-	4.70	-

Although the coloration of the three crystal types is different, there exists a certain similarity between the absorption bands. The two bands between 2.06 and 2.17 ev and 3.14 and 3.29 ev seem to be common to all three crystals. A temperature decrease always shifts the first band to lower and the second one to higher energies. The Mollwo α and β bands seem to be identical with these two bands, according to their temperature dependence and photochemical bleaching.¹⁴⁾ If so, the four bands of Crystal No. 1 can be considered as color-center bands caused by vacancies in CaF_2 crystal lattice and not directly by impurities.

It is a pleasure to thank V. Sils for the help in preparation of the samples, W. B. Westphal for conductivity measurements, and K. A. Wright, High Voltage Research Laboratory, M.I.T., for the coloration of crystals with high-energy electrons.

14) A. Smakula, Phys. Rev. 91, 1570 (1953).

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