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EFFECT OF PLASTIC DEFORMATION ON COLOR CENTERS IN SODIUM CHLORIDE CRYSTAL*

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Introduction

In a series of investigations[1,2,3,4], the author demonstrated the effect of plastic deformation on color centers in alkali halide crystals by measuring the absorption spectra, and revealed that: (1) Plastic deformation caused negligible bleaching of electrolytically produced F centers in NaCl and KCl, but bleached those in KBr and KI. The F centers in deformed KCl, KBr and KI crystals were spontaneously bleached on storage in the dark at room temperature, and the bleaching of the F centers by the irradiation with white light was more rapid for the deformed crystals than for the undeformed crystals. The bleaching of the F centers was accompanied by the formation of broad bands on the longer wavelength side[1]. (2) Plastic deformation shifted the colloid band of NaCl from the initial peak position to the longer wavelength side when measured parallel and to the shorter wavelength side when measured normal to the direction of compression, that is, the deformation made the NaCl crystal containing colloid centers dichroic. Storage in the dark or annealing at 100~200°C shifted the band back towards the initial band peak, and annealing at 200°C made the parallel and normal spectra identical. The higher pressure caused a greater deformation of colloid particles and in consequence a greater peak shift of colloid band[2,4]. (3) Colorability in deformed NaCl crystal was examined by the irradiation with γ-rays from Co^{60}. The F center formation in deformed crystal was markedly increased and broad absorption band was formed on the long wavelength side. The F centers were rapidly bleached by the exposure to F light, changing the color from dark yellow to blue[3]. (4) Plastic deformation bleached the F centers produced by γ-ray irradiation from Co^{60}. Subsequent exposure to F light caused a very rapid bleaching of the F centers[3].

In this investigation the dichroism induced by plastic flow of sodium chloride crystal containing colloid centers with or without F centers, is studied by measuring the absorption spectra with polarized light. The annealing effect on the colloid and F centers in deformed crystals is also examined. The plastic deformation is carried out at room temperature by the uniaxial compression with a pressure of about 500 kg/cm^2, instead of the die-casting method used in the previous investigations.

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* *This investigation has been done by F. Okamoto, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) R. Kiyama and F. Okamoto, *This Journal*, **25**, 1 (1955)
2) R. Kiyama and F. Okamoto, *ibid.*, **25**, 6 (1955)
3) R. Kiyama and F. Okamoto, *ibid.*, **25**, 49 (1955)
4) R. Kiyama, *ibid.*, **26**, 35 (1956)

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Experimentals

Preparation of samples Sodium chloride crystals containing colloid and F centers were prepared by means of electrolysis with a pointed cathode of nichrome and a flat anode of graphite in the furnace of 650°C. It is known[5,6] that the F centers in NaCl crystal coagulate to the colloids more easily than those in potassium salts. Therefore, the concentration ratio of colloid center to F center, and the peak position of colloid band were sensitively influenced by the cooling velocity after electrolysis. In this investigation the specimens which contain pure colloid centers, pure F centers and colloid centers which coexist with small or large concentrations of F centers, were used.

Procedure The colored crystal cleaved to a cubic form of about $5\times5\times5\,mm^3$ was deformed uniaxially with a pressure of about $500\,kg/cm^2$. The strain introduced in the crystal was about 8～10% in the direction of compression. The strains normal to the direction of compression, a and b, were different from each other. Usually one direction was elongated much more than the other. The crystal dimensions before and after compression and the strains introduced are given in Table 1. After the deformation three crystal plates, A, B and C of about 2 mm thick

Table 1 Crystal dimension and strain introduced

	Crystal dimension (mm)		Strain %	Corresponding Fig. No.
	before compression	after compression		
la	5.53	6.05	+ 9.4	
lb	5.50	5.65	+ 2.7	2
lc	5.41	4.91	− 9.2	
la	5.15	5.63	+ 9.3	
lb	5.13	5.24	+ 2.1	3
lc	5.16	4.63	−10.3	
la	5.49	5.97	+ 8.7	
lb	5.86	5.99	+ 2.2	4
lc	5.76	5.26	− 8.7	
la	5.31	5.65	+ 6.4	
lb	4.81	5.10	+ 6.0	5
lc	4.76	4.38	− 8.0	

were cleaved along {100} planes of the compressed specimen as illustrated in Fig. 1.

The absorption measurements were carried out on each plate A, B or C by using polarized light, over the wavelength range from 400 to 1000 mμ at room temperature, on each step of the successive treatments as follows: (i) before deformation, (ii) immediately after deformation, (iii) after storage in the dark, and (iv) after annealing in the dark. The direction of the polarization

5) F. Seitz, *Rev. Mod. Phys.*, 26, 42 (1954)
6) A. B. Scott, W. A. Smith and M. A. Thompson, *J. Phys. Chem.*, 57, 757 (1953)

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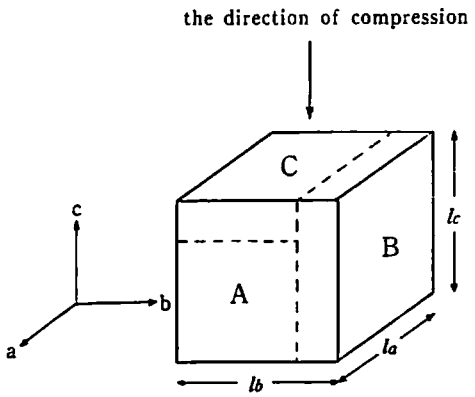


Fig. 1 The cutting of the compressed specimen and the direction of the polarization of the light for the absorption measurements

A, B, C: crystal plate cut from the compressed specimen
a, b, c: direction of the polarization of the light for the absorption measurements
la, *lb*, *lc*: length of cube edges of the specimen

of the light in each measurement is denoted by the subscript a, b or c on each curve in Figs. 2, 3 and 4. In these measurements the uncolored crystal subjected to the same treatments as for the colored crystal, was used as the blank crystal.

Results

Effect of plastic deformation on colloid centers Plastic deformation shifted colloid band from the initial peak position to the longer wavelength side when measured with polarized light normal and to the shorter wavelength side when measured with polarized light parallel to the direction of compression, increasing the band width and decreasing the band height (curve 2 in Figs. 2, 3 and 4). The amount of peak shift depended on the strain introduced. A greater strain caused a greater peak shift. On the storage in the dark the shifted bands returned towards the initial band peak with an increase in band height (curves 3 and 4 in Fig. 3). Annealing at 200°C for 4 hours and at 300°C for 1.5 hours made the shifted bands almost identical (curves 4, 6 and 3 in Figs. 2, 3 and 4 respectively). The annealing caused considerable bleaching of the color from the outer part of the crystal. The final peak position after annealing was located on the shorter wavelength side of the initial one. In the case shown in Fig. 4, the initial peak position of the colloid band could not be decided exactly because of the overlap with large F band. However, the true peak position is undoubtedly located on the longer wavelength side than 560 mμ which is noted in the figure, and it may be deduced as in the case of Figs. 2 and 3 that the colloid band shifts to the shorter wavelength side on the annealing.

Effect of plastic deformation and annealing on F centers The results on the crystal containing only F centers are shown in Fig. 5. Plastic deformation and subsequent storage in the dark did not change the F band shape, and the crystal did not show the dichroism (curves 1, 2 and 3 in Fig. 5). Annealing at 200°C for 2 hours in the dark changed the band shape considerably, decreasing the F band height and forming the band on the longer wavelength side which had a peak at 694 mμ (curve 4). Further 2 hours annealing at 200°C decreased both F and 694 mμ bands, increasing the absorption in the region between these two bands (curve 5). By annealing at 300°C for 1.5 hours, the F band almost disappeared and another band was formed at 573 mμ (curve 6). In the outer part of the crystal the bleaching of the F centers was very

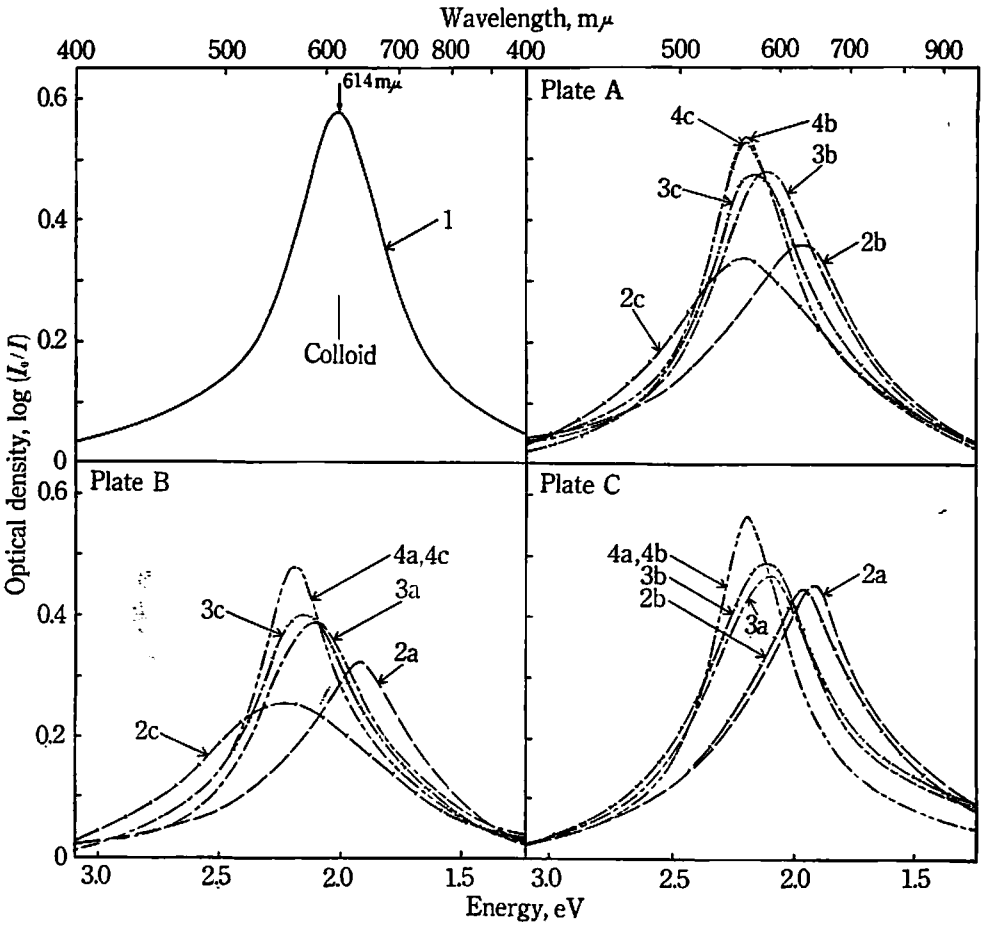
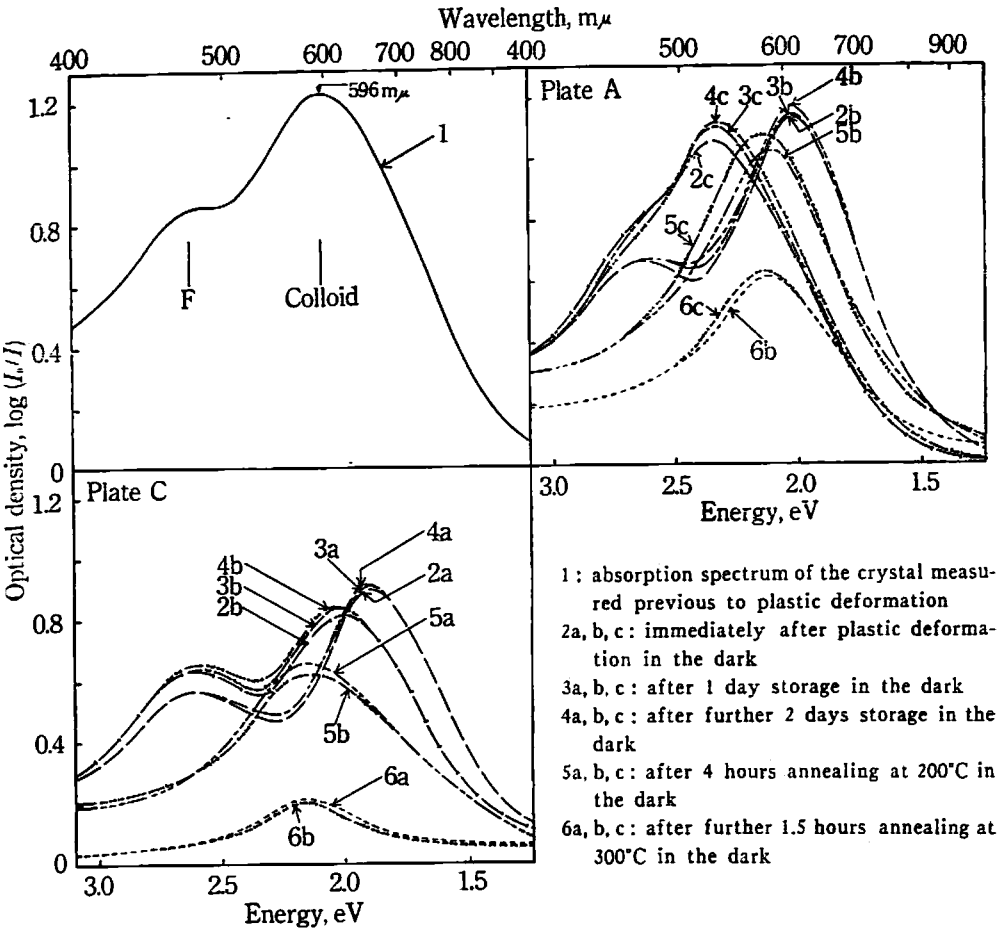


Fig. 2 Changes of the absorption spectrum of colloid centers in NaCl crystal after plastic deformation (Measurements were carried out on the crystal plates, A, B and C with polarized light, a, b and c.) pressure=450 kg/cm², crystal thickness=1.8 mm

1 : absorption spectrum of the crystal measured previous to plastic deformation
2a, b, c : immediately after plastic deformation in the dark
3a, b, c : after 4 hours annealing at 200°C in the dark
4a, b, c : after further 1.5 hours annealing at 300°C in the dark

plate	curve	peak wavelength of colloid band	plate	curve	peak wavelength of colloid band	plate	curve	peak wavelength of colloid band
A	2b	630 mμ	B	2a	642 mμ	C	2a	645 mμ
	3b	585		3a	588		3a	588
	4b	563		4a	565		4a	563
	2c	559		2c	556		2b	630
	3c	570		3c	575		3b	584
	4c	563		4c	565		4b	563

rapid and the growth of the band on the longer wavelength side was very slight when annealed at 200°C, and the 573 mμ band was not formed predominantly when annealed at 300°C (curves



1 : absorption spectrum of the crystal measured previous to plastic deformation
2a, b, c : immediately after plastic deformation in the dark
3a, b, c : after 1 day storage in the dark
4a, b, c : after further 2 days storage in the dark
5a, b, c : after 4 hours annealing at 200°C in the dark
6a, b, c : after further 1.5 hours annealing at 300°C in the dark

Fig. 3 Changes of the absorption spectrum of colloid and F centers in NaCl crystal after plastic deformation (Measurements were carried out on the crystal plates, A and C with polarized light, a, b and c.) pressure=520kg/cm², crystal thickness=2.4 mm

plate	curve	peak wavelength of colloid band	plate	curve	peak wavelength of colloid band
A	2b	611 mμ	C	2a	654 mμ
	3b	610		3a	653
	4b	610		4a	649
	5b	587		5a	577
	6b	584		6a	575
	2c	530		2b	620
	3c	532		3b	610
	4c	534		4b	609
	5c	578		5b	581
	6c	580		6b	575

4′, 5′ and 6′).

In the case of the F centers coexisting with colloid centers, the F band shape seems to be changed slightly by the deformation (curves 2 in Figs. 3 and 4), but it may be considered that

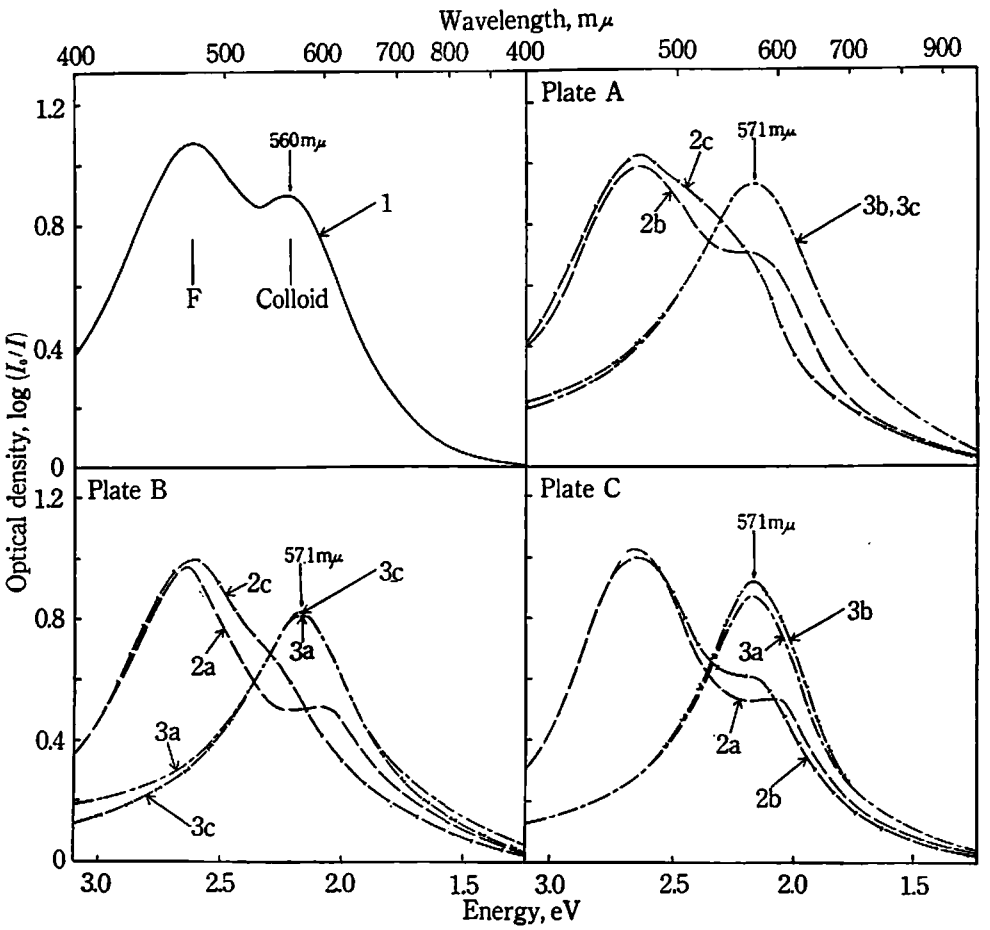


Fig. 4 Changes of the absorption spectrum of colloid and F centers in NaCl crystal after plastic deformation (Measurements were carried out on the crystal plates, A, B and C with polarized light, a, b and c.) pressure=430 kg/cm², crystal thickness=2.0 mm

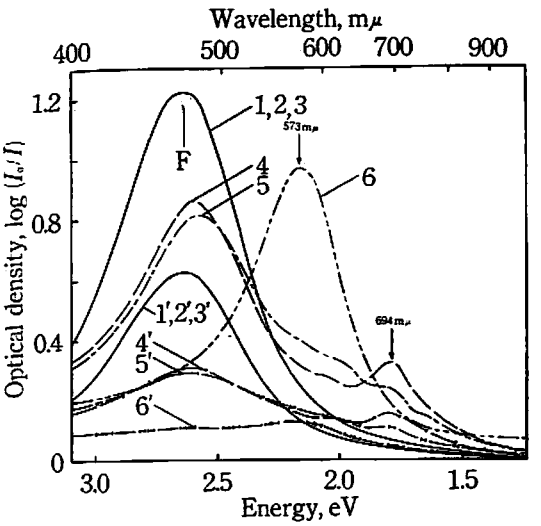
1 : absorption spectrum of the crystal measured previous to plastic deformation
2a, b, c : immediately after plastic deformation in the dark
3a, b, c : after 4 hours annealing at 200°C in the dark

this change is due to the shift of colloid band and not to that of the F band by the deformation.

The F centers in undeformed crystal were more stable than those in deformed crystal when annealed at 200°C, that is, the bleaching of the F centers and the formation of the band on the longer wavelength side were very slight as shown in Fig. 6 (curves 3 and 4). Annealing at 300°C for 1.5 hours formed a band at 567 mμ (curve 5).

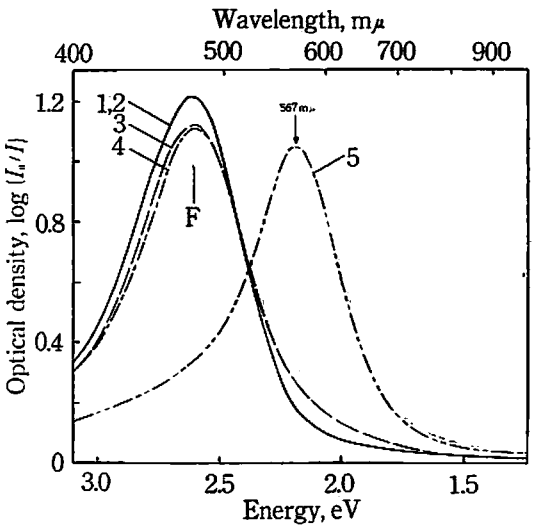
Considerations

When the crystal containing colloid centers was deformed the crystal became dichroic, and when the crystal was annealed the dichroism disappeared. The result indicates that all the spherical



1 and 1′: absorption spectrum of the crystal measured previous to plastic deformation
2 and 2′: immediately after plastic deformation in the dark
3 and 3′: after 1 day storage in the dark
4 and 4′: after 2 hours annealing at 200°C in the dark
5 and 5′: after further 2 hours annealing at 200°C in the dark
6 and 6′: after further 1.5 hours annealing at 300°C in the dark

Fig. 5 Changes of the absorption spectrum of F centers in NaCl crystal after plastic deformation pressure=530 kg/cm², crystal thickness=4.4 mm
(Superscript′ denotes the measurement of the outer part of the crystal, where crystal thickness was 2.3mm.)



1: absorption spectrum of the crystal containing F centers
2: after 1 day storage in the dark
3: after 2 hours annealing at 200°C in the dark
4: after further 2 hours annealing at 200°C in the dark
5: after further 1.5 hours annealing at 300°C in the dark

Fig. 6 Changes of the absorption spectrum of F centers in undeformed NaCl crystal after storage and annealing crystal thickness=4.4 mm

colloid particles are deformed to the parallel-oriented ellipsoidal shapes by uniaxial compression and the deformed colloid particles recover to the initial spherical shapes on storage and annealing as illustrated in the previous paper[2]. As in the present investigation polarized light was used instead of natural light, more detailed absorption spectra were obtained. In the previous investigation a spectrum which had the band peak on the shorter wavelength side was observed when measured normal to the direction of compression with natural light. On the other hand, polarized

light resolved the spectrum into two bands, one which had the band peak on the longer wavelength side and the other on the shorter wavelength side. This result may be ascribed to the measurements along the longer and the shorter axes of deformed ellipsoidal colloid particles respectively, and confirms the ellipsoidal shape of the deformed colloid particles. Annealing at 200 and 300°C shifted the colloid band to the shorter wavelength side of the initial one. This may be due to a reduction in size of colloid particles on the annealing. The F band which existed previously, almost disappeared on the annealing as shown in Figs. 3 and 4. It is assumed on the basis of the experimental result on pure F centers shown in Fig. 5 that some of the F centers bleached and some of them coagulated to the colloids by the annealing.

When the deformed crystal containing F centers was annealed at 200°C for 2 hours in the dark, broad bands were formed on the longer wavelength side of F band, showing a peak at 694 mμ (Fig. 5). These bands are probably R_1, R_2 and M bands because of their locations and band shapes. The result that R_1, R_2 and M bands are formed easily by annealing in the dark after deformation, may be ascribed to the large density of clusters of positive- and negative-ion vacancies which are formed during plastic flow. The band at about 570 mμ which was formed by annealing the crystal containing F centers at 300°C, may be a colloid band from the condition of the formation and the location of the band.

When the crystal containing colloid and F centers is deformed, the colloid band shifts to longer or shorter wavelength sides in accordance with the strain introduced in the crystal, whereas the F band does not shift. The different character between the two bands is useful to distinguish colloid center from F center in the crystal where the origin of coloration is unknown. For instance, the origin of the coloration of the violet and the blue rocksalt has been disputed among many investigators for a long time, and it is pointed out from the result of the experiments using ultramicroscope that the coloration can be associated partly with F, R and occasionally M centers and partly with colloidal particles[7]. If plastic deformation is applied to the rocksalt as mentioned above, it will be very useful to confirm the origin of the coloration.

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7) K. Przibram, *Irradiation Colours and Luminescence*, Pergamon Press Ltd., London, Chap. 12 (1956)