The Review of Physical Chemistry of Japan Vol. 24 No. 1 (1954)

THE AFTER-EFFECT OF HYDROSTATIC PRESSURE ON THE F-BANDS IN ALKALI HALIDES*

By Shigeru Minomura

Introduction

As ionic crystals, such as alkali halides, have plastic property, if the crystals are compressed by hydrostatic pressure for a certain hours, the deformation of the crystals by the motion of the neighbouring lattice sites of the lattice imperfections will occur and the strain exists still after releasing the pressure. In order to confirm the model of the F-center and the interpretation of the effect of temperature and pressure on the character of the F-bands which has been cited in the literature, the author has investigated the influence of the residual stress on the F-bands formed in alkali halides by an exposure to $RaBr_2$. The model of the F-center formed in alkali halide crystals by X-ray irradiation, neutron or electron bombardment, or adding a stoichiometric excess of alkali metal assumes that an electron is bound to a lattice imperfection in the crystals 1)~6) and the bell-shaped absorption band is attributed to the electronic transition ($1s$—$2p$ transition) between these states 7)~12).

The peak wavelength, the absorption coefficient, and the width at half maximum of the F-band are variable with temperature and pressure, as well as impurity content. The position of the peak shifts to the short wavelength with decreasing temperature 13)~

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* *A part of this investigation was published by R. Kiyama and S. Minomura in Proc. Japan Acad.*, **30**, No. 3, 199 (1954) (*Communicated S. Horiba, M. J. A.*, March 12, 1954).

1) R. W. Pohl, *Proc. Phys. Soc.*, **49**, 3 (1937)
2) A. Smakula, *Z. Phys.*, **55**, 289 (1929); **59**, 603 (1930); **63**, 762 (1930)
3) F. Seitz, *Rev. Mod. Phys.*, **18**, 384 (1936)
4) N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals* (Oxford University Press, London, 1940) Chap. 4
5) G. Heiland, Z. Phys., **127**, 144 (1950)
6) C. J. Delbecq and P. Pringsheim, *J. Chem. Phys.*, 21, 794 (1953)
7) S. R. Tibbs, *Trans. Faraday Soc.*, **35**, 1471 (1939)
8) R. Kubo, *J. Phys. Soc. Japan*, **3**, 254 (1948); **4**, 322, 326 (1949)
9) J. H. Simpson, *Proc. Roy. Soc.*, A **197**, 269 (1949)
10) T. Inui and Y. Uemura, *Progr. Theoret. Phys.*, **5**, 252, 395 (1950)
11) L. Pincherle, *Proc. Phys. Soc.*, A **64**, 648 (1951)
12) J. A. Krumhansl and N. Schwartz, *Phys. Rev.*, **89**, 648 (1951)
13) E. Mollwo, *Z. Phys.*, **85**, 56 (1933)
14) H. F. Ivey, *Phys. Rev.*, **72**, 341 (1947)
15) T. Muto, *Progr. Theoret. Phys.*, 4, 181, 243 (1949)
16) K. Huang and A. Rhys, *Proc. Roy. Soc.*, A **204**, 406 (1950)
17) T. Nagamiya, *J. Phys. Soc. Japan*, **7**, 354 (1952)

[19] and increasing pressure[20],[21]. The shift is interpreted by the variation of the radius of the potential well of the halogen-ion vacancy to which an election is bound, or the change of the interaction of the F-center electron with lattice vibration. Mollow[13] has indicated the empirical relation that the peak wavelength of the F-band is approximately proportional to the square of the interionic distance for various alkali halides at room temperature. Inui and Uemura[10] have reported that the principal cause of the shift of the peak of the F-band with temperature is the thermal expansion of the lattice, and that if the displacement of the most neighbouring alkali metal ions of the vacant lattice site by the thermal expansion is greater than that of the perfect lattice by the factor of 1.5, the calculated shift is approximately in accord with the experimental data. On the other hand, Burstein, Oberly and Davisson[20], and Jacobs[21] have measured the shift of the peak of the F-band to the short wavelength with hydrostatic pressure and have indicated that the shift may be due to the fact that the F-center electron exerts a considerably smaller repulsion on its neighbours than the halogen ion at the normal position in the lattice, so that the neighbouring alkali metal ions are displaced from their normal positions in the lattice towards the electron.

Smekal[2] and Schroeder[22] have found that the crystals colored by X-rays are bleached by the application of uniaxial stress which is near the elastic limit. Seitz[23] has explained the bleaching effect of the cold work by the assumption that the region about the vacancies associated with the color centers becomes heated when a dislocation passes very close and that F-center electrons and positive holes evaporated and have an opportunity to recombine. It is known that rubidium halides, except the fluoride, undergo a polymorphic transition (NaCl type→CsCl type) at room temperature and about 5000 atm.[24]~[26] Jacobs[21] has investigated the effect of the structure transformation in the rubidium halides on the F-bands and indicated that the F-bands just after the transformation locate in the pretransition positions, but decrease in height by 40 % and that the bleaching effect of a plastic deformation accompanied with uniaxial stress is ascribed to the structure transformation in the crystals. At the same time, he has found that for the other alkali halides of NaCl type which do not make the structure transformation under the experimental conditions, the widths of the F-bands do not change with pressure within a scatter of 2 or 3 %. Przibram[27], Smakula[2] and Rexer[28]

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[18] M. Rax, *J. Chem. Phys.*, **20**, 1752 (1952)
[19] R. C. O'Rourke, *Phys. Rev.*, **91**, 265 (1953)
[20] E. Burstein, J. J. Oberly and J. W. Davisson, *ibid.*, **85**, 729 (1952)
[21] I. S. Jacobs, *ibid.*, **93**, 993 (1954)
[22] H. J. Schroeder, *Z. Phys.*, **76**, 608 (1932)
[23] F. Seitz, *Phys. Rev.*, **80**, 239 (1950)
[24] J. C. Slater, *ibid.*, **23**, 488 (1924)
[25] P. W. Bridgman, *Z. Krist.*, **67**, 363 (1928)
[26] R. B. Jacobs, *Phys. Rev.*, **54**, 468 (1938)
[27] K. Przibram, *Z. Phys.*, **41**, 833 (1927), **68**, 403 (1931)
[28] E. Rexer, *ibid.*, **75**, 777 (1932); *Phys. Z.*, **33**, 202 (1932)

have found that the coloring of alkali halide crystals increases remarkably with a plastic flow. Seitz[23] has offered the interpretation that the influence of a plastic flow on the coloring can probably be due to the large density of clusters of positive- and negative-ion vacancies which are formed during a plastic flow.

The author has investigated for five alkali halides (LiF, NaCl, KCl, KBr, and KI) and has reported the broadening of the peaks of the F-bands and the decrease of the spontaneous bleaching, after the application of hydrostatic pressures (2500, 5000, and 7500 atm) on the crystals colored by an exposure to $RaBr_2$, and the coloring of the crystals after the application of hydrostatic pressure (7500 atm). The results have been compared with other elastic stiffness and the plastic properties in the crystals have been considered.

Experimentals

Preparation of samples Large single crystals of five alkali halides (LiF, NaCl, KCl, KBr, and KI) used in this investigation were synthesized from the commercial reagents made in Japan. The method of crystal growth, the chemical purity, and some physical properties of LiF have been published in the previous paper[29]. The other alkali halides were synthesized by the same method as in the case of LiF and the impurity contents of the reagents are shown in Table 1. The specimens of each compound were cleaved from a part of the same single crystal block and polished in a certain thickness (3.6 mm for LiF, NaCl, KCl, KI and 3.1 mm for KBr), so that the specimens had the same impurity content, thermal treatment, mechanical history, and other factors.

Table 1 The impurities (in %) of alkali halide reagents

Impurities Crystals	Cl	Br	I	SO_4	PO_4	IO_3	S_2O_3	CN
NaCl	HCl 0.003	0.01	0.002	0.002	0.0005	——	——	——
KCl	HCl 0.003	0.01	0.002	0.003	0.002	——	——	——
KBr	0.1	BrO_3 0.001	0.005	0.005	0.003	——	——	——
KI	0.001	0.001	——	0.001	0.005	0.0003	trace	0.0005

Impurities Crystals	Pb	Fe	Mg	Ca	Ba	K	Na	N
NaCl	0.0005	0.0003	0.001	0.003	0.001	0.005	——	0.001
KCl	0.0005	0.0003	0.0005	0.001	0.001	trace	about 0.02	0.001
KBr	0.0005	0.0005	0.001	0.001	0.002	K_2CO_3 0.007	about 0.02	0.0005
KI	0.0005	0.0003	0.001	0.001	0.001	K_2CO_3 0.01	about 0.03	0.001

The specimens were arranged on the circle of the radius 20 mm and colored by an exposure to 5 mg $RaBr_2$ which was set at the center of the circle in the dark at room

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[29] R. Kiyama and S. Minomura, *This Journal*, **21**, 69 (1951); **23**, 10 (1953)

temperature (6~23°C). $RaBr_2$ was rotated by a fixed angle at the certain intervals to color the specimens in the same concentration.

Apparatus The high pressure apparatus for the application of hydrostatic pressure on the specimens is the same as in the previous paper[30]. In order to measure the absorption spectra of the specimens a Beckman Model DU Quartz Spectrophotometer was used.

Procedure The following two series of the experiments were performed. Exp. 1: the virgin specimens of the five alkali halides (LiF, NaCl, KCl, KBr, and KI) were colored by an exposure to $RaBr_2$ for 49, 61, 62, 69, and 84 days respectively. The colored specimens were compressed in mobil oil at room temperature and at 2500, 5000, 7500 atm for 1 hour and at 7500 atm for 24 hours. After their compressing the specimens were washed with petroleum ether. It was confirmed by the absorption measurement that the mobil oil was washed out from the surface of the specimens. Exp. 2: the virgin specimens of the five alkali halides and the specimens compressed at 7500 atm for 24 hours were colored by an exposure to $RaBr_2$ for 45, 72, 45, 46, and 98 days respectively.

The absorbance of the specimens, $\log_{10}(I_0/I)$, where I_0 is the light transmitted through the specimens after coloring and compressing, was measured over a range embracing the whole F-band at room temperature (10~23°C). The individual measuring points in the vicinity of the peaks of the F-bands in the five alkali halides were plotted against the wavelengths at the intervals of 0.25, 1.0, 1.0, 2.5, and 5 mμ respectively, which were equal to a half grade of the wavelengths notched in the spectrophotometer.

Alkali halide crystals colored by an exposure to $RaBr_2$ were bleached in the dark at room temperature. The compounds which show the peaks of the F-bands at the longer wavelengths are more easily bleached. KCl, KBr, and KI just after the exposure to $RaBr_2$ were remarkably bleached, but bleached so scarcely after the lapse of 24 hours from the end of the exposure to $RaBr_2$ that their absorption spectra could be determined. The lapse of time taken from the end of the exposure to $RaBr_2$ to the spectral measurement was specified on the F-bands in each compound shown in the figures. The sampling for the compression and the spectral measurement was conducted under the light transmitted through a red filter (a green filter for Exp. 2 of KI).

Results

The broadening of the peaks of the F-bands The results of Exp. 1 are shown in Figs. 1~5 and the detail in the vicinity of the peaks of the F-bands in LiF of Fig. 1 is shown in Fig. 6. The applied pressures, the compressing time and the time taken from the end of the exposure to $RaBr_2$ to the spectral measurement are specified on each F-band in these figures. The agreement of the peak wavelengths of the F-bands formed in the virgin specimens with those cited in the literature[1][6][17][21][31][32] is reasonably satis-

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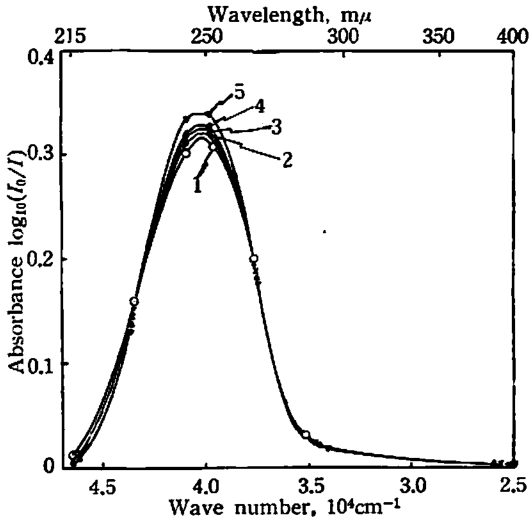
[30] R. Kiyama and S. Minomura, *This Journal*, 22, 4, 9 (1952)

[31] R. Ottmer, *Z. Phys.*, 46, 812 (1928)

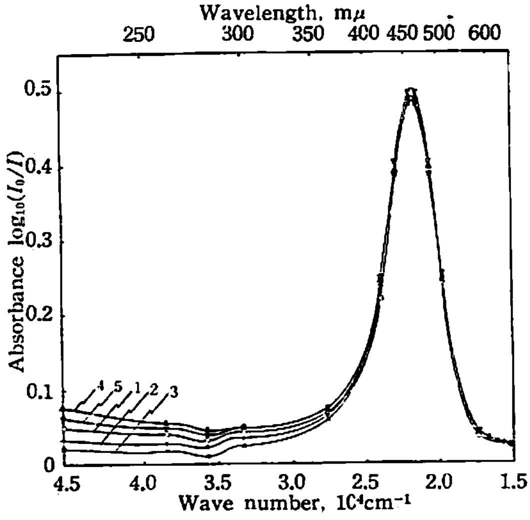
[32] A. Glasner and F. C. Tomkins, *J. Chem. Phys.*, 21, 1817 (1935)



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		2
2	—+—+—	2500	1	2
3	—×—×—	5000	1	2
4	—△—△—	7500	1	2
5	—▽—▽—	7500	24	26

Fig. 1 F-bands in LiF at about 11°C compressed after coloring

factory. Because the sampling for the compression and the spectral measurement in the experiment of KI shown in Fig. 5 was conducted under the light transmitted through a red filter (the F-light of KI), the R-bands were created in the long wavelength tail of the F-band, as Pringsheim[33], Petroff[34] and many other investigators have reported. Therefore, the position (720 mμ) of the peak of the F-band formed in the virgin specimens which is pointed by an arrow is at the longer wavelength in comparison with that (695 mμ) of KI in Fig. 12 and it is made indistinguishable by the R-band. The peaks of the F-bands after compressing are broadened, although before compressing a single point can be decided as the peak. The broadening increases with increasing pressure and compressing time. The peaks of the F-bands in LiF and NaCl are slightly broadened from the position before compressing to the long wavelength, but the phenomenon has not been found in the other crystals. The peak wavelengths of



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		26
2	—+—+—	2500	1	26
3	—×—×—	5000	1	26
4	—△—△—	7500	1	26
5	—▽—▽—	7500	24	26

Fig. 2 F-bands in NaCl at about 22°C compressed after coloring

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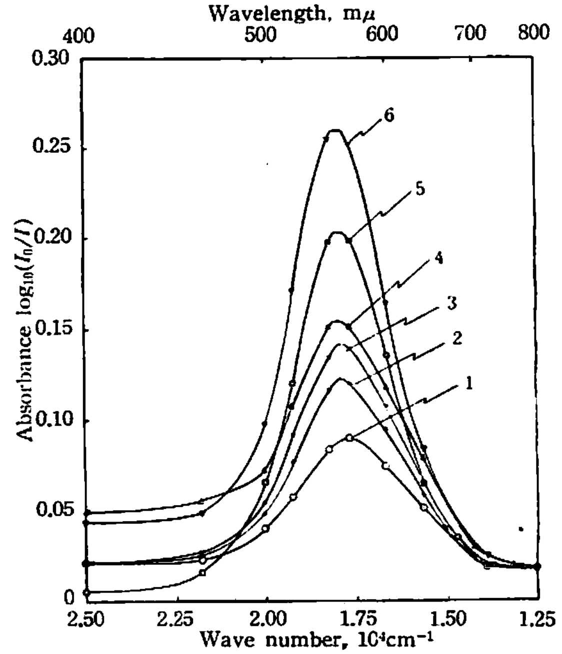
33) R. Casler, P. Pringsheim, and Y. Yuster, *J. Chem. Phys.*, 18, 1564 (1950)

43) S. Petroff, *Z. Phys.*, 127, 443 (1950)

the F-bands of Figs. 1~5 are shown in Table 2. The shift in the wave number from the peak before compressing to the short wavelength edge in the broadening of the peaks after compressing is in the order of LiF > NaCl ≈ KCl* ≈ KBr > KI under a desired pressure.

The vicinity of the peak of the F-band formed in the virgin specimen of LiF by an exposure to $RaBr_2$ for 45 days and the variation of that in the same specimen compressed at 7500 atm for 24 hours with the lapse of days (2~22 days) are shown in Fig. 7. The broadening of the peak by compressing diminishes gradually from the short wavelength edge with the lapse of days and disappears completely after the lapse of 22 days from compressing and the peak wavelength is in accordance with that before compressing.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—+—+—	2500	1	24
3	—×—×—	5000	1	24
4	—△—△—	7500	1	24
5	—⊡—⊡—	7500	24	72
6	—▽—▽—	7500	24	48

Fig. 3 F-bands in KCl at about 10°C compressed after coloring

Table 2 The peak wavelengths of the F-bands in alkali halides at room temperature

Applied pressures atm	Compressing hours	LiF	NaCl	KCl	KBr	KI
		about 11°C	about 22°C	about 10°C	about 10°C	about 22°C
1		249.0 mμ	465 mμ	560 mμ	626 mμ	720 mμ
2500	1	248.0~250.3	463~466	557~560	622~625	——
5000	1	247.0~250.4	461~466	554~558	619~625	712~720
7500	1	246.5~250.4	459~466	552~556	616~625	708~720
7500	24	245.5~250.6	458~467	550~560	——	——

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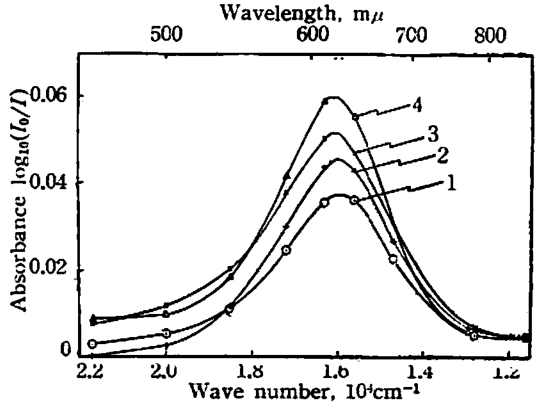
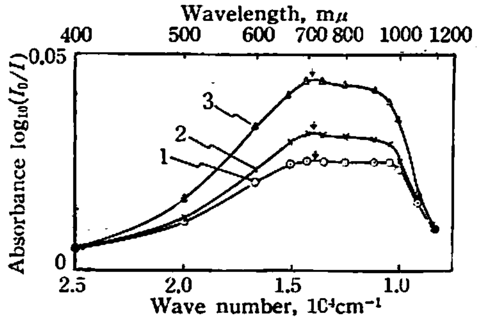
* In the previous paper, *Proc. Japan Acad.*, **30**, No. 3, 199 (1954), the peak wavelength of the F-band formed in the virgin specimen of KCl has been reported as 566 mμ, but the value is replaced by 560 mμ, so that the order of the compounds by the shifts in the wave number is LiF > KCl ≈ KBr.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—+—+—	2600	1	24
3	—×—×—	5000	1	24
4	—△—△—	7500	1	24

Fig. 4 F-bands in KBr at about 10°C compressed after coloring

The decrease of the spontaneous bleaching Alkali halide crystals colored by an exposure to $RaBr_2$ are bleached in the dark at room temperature. The rate of the spontaneous bleaching decreases with the lapse of time taken from the end of the exposure to $RaBr_2$ and with increasing pressure applied on the specimens. The F-bands in each compound shown in Figs. 1~5 increase with increasing pressure, in spite of a certain lapse of time from the end of the exposure to $RaBr_2$.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—×—×—	5000	1	24
3	—△—△—	7500	1	24

Fig. 5 F-bands in KI at about 22°C compressed after coloring

The coloring after compressing The results of Exp. 2 are shown in Figs. 8~12. The concentration of the F-centers formed in the specimens after the application of hydrostatic pressure is larger than that formed in the virgin specimens. The number N of the F-centers, in units of cm^{-3}, can be calculated from the following relationship derived by Smakula[2] between the absorption coefficient $\alpha_{\max}$ at the peak wavelength, in units of cm^{-1}, and the width at half maximum of the F-band W, in units of electron volts,

$$Nf=\frac{18m}{\pi e^2 h}\frac{n}{(n^2+2)^2}\alpha_{\max}W=1.31\times10^{17}\frac{n}{(n^2+2)^2}\alpha_{\max}W,$$

where e, h and m are the usual atomic constants, n is the index of refraction of the crystal for the F-light, and f is the oscillator strength of the F-centers (0.7 for NaCl, 0.81 for KCl[35] and the author assumed unity for the other compounds). The values of n given from the experimental curves by Gyulai[36] between the wavelength and the index of

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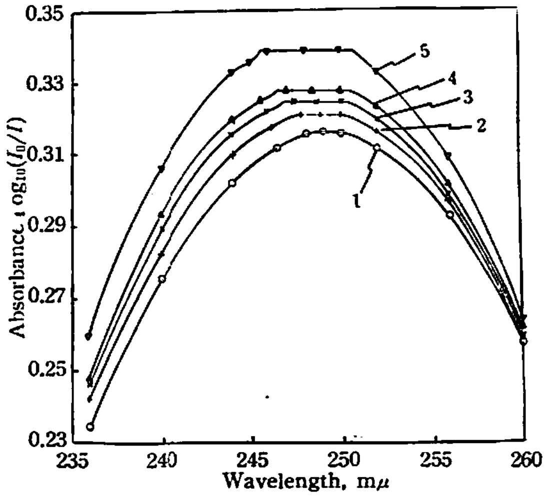
35) F. Seitz, *Rev. Mod. Phys.*, **18**, 384 (1946)

36) Z. Gyulai, *Z. Phys.*, **40**, 80 (1928)

refraction and the concentrations of the F-centers formed in the virgin specimens (N_1) and those formed in the specimens after compressing at 7500 atm for 24 hours (N_{7500}) and the ratio of both concentrations (N_{7500}/N_1) are shown in Table 3. N_{7500}/N_1 increases in the order of LiF<NaCl<KI<KCl<KBr.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to RaBr₂
1	—⊙—⊙—	1		2
2	—+—+—	2500	1	2
3	—×—×—	5000	1	2
4	—△—△—	7500	1	2
5	—▽—▽—	7500	24	26

Fig. 6 Peaks of F-bands in LiF at about 11°C compressed after coloring

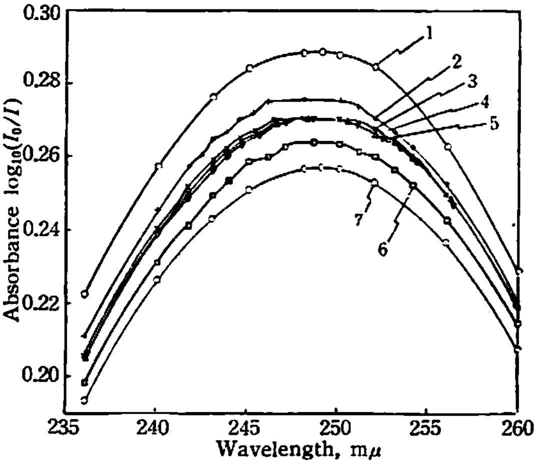
The broadening of the peaks to the short wavelengths is not found in the F-bands formed by an exposure to $RaBr_2$ over 45 days after compressing, but found in the F-bands formed by the exposure within 10 days after compressing.

Table 3 The index of refraction (n) and the concentration (N_1,N_{7500}) of the F-centers in alkali halide

	LiF	NaCl	KCl	KBr	KI
n	1.418	1.556	1.491	1.555	1.648
N_1, $10^{16}\,cm^{-3}$	1.47	2.68	0.76	1.04	1.01
N_{7500}, $10^{16}\,cm^{-3}$	1.52	3.14	1.06	3.49	1.35
N_{7500}/N_1	1.03	1.17	1.39	3.36	1.34

Considerations

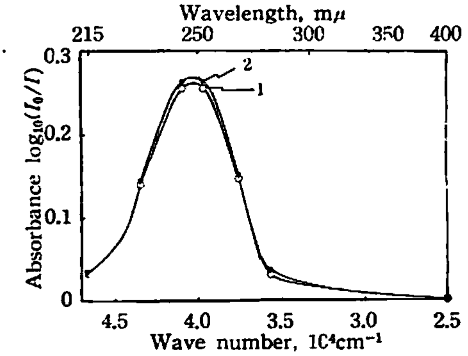
If the shifts of the peaks of the F-bands to the short wavelengths with hydrostatic pressure are attributed to the displacement of the neighbouring alkali metal ions of the vacant lattice sites from their normal positions in the lattice towards the F-center electrons, the broadening of the peaks to the short wavelengths after the application of hydrostatic pressure is ascribed to the fact that a part of the neighbouring alkali metal ions has restored their normal positions from the displaced positions and the other part is on the way to their normal positions, so that the absorption spectra in both cases overlap. The diminution of the broadening of the peaks with the lapse of days is due to the fact that the neighbouring alkali metal ions gradually restore from the displaced positions. Jacobs[21] has indicated that the shifts of the peak wave numbers of the F-bands



Curves No.	Legends	Pressures atm	Compressing hours	Days after the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		0
2	—+—+—	7500	24	2
3	—×—×—	〃	〃	4
4	—△—△—	〃	〃	7
5	—▽—▽—	〃	〃	10
6	—⊡—⊡—	〃	〃	15
7	—⊙—⊙—	〃	〃	22

Fig. 7 Peaks of F-bands in LiF compressed after coloring

in alkali halides with pressure depend almost entirely on the crystallographic unit cell distance which is calculated from the compressibility. The magnitude of the shifts for the unit wave number, $\log_{10}(\nu/\nu_0)$, where ν_0 is the peak wave number of the F-band formed in the virgin specimen and ν is the wave number of the short wavelength edge of the peak broadened by compressing, and the stress in atm for the shifts which are given from the experimental curves by Jacobs showing the dependence of the peak wave number on the lattice parameter calculated from the compressibility data by Slater[24] are shown in Table 4. The residual stress in the specimens compressed for 1 hour indicates the values of 21~34 % of the pressures applied on the specimens, and that compressed for 24 hours indicates the values of about



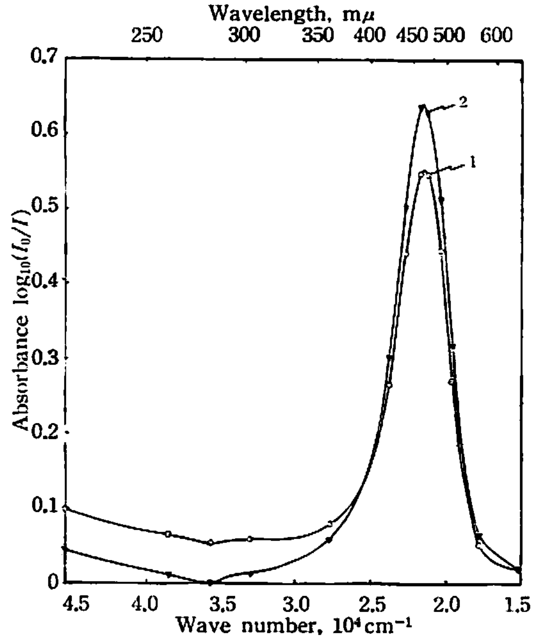
Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		2
2	—▽—▽—	7500	24	2

Fig. 8 F-bands in LiF at about 11°C colored after compressing

Table 4 The shifts by pressure and the residual stress

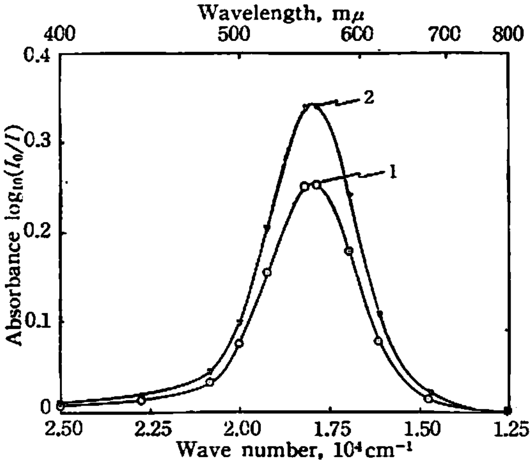
Applied pressures atm	Compressing hours	Crystals / Shift-stress	LiF	NaCl	KCl	KBr	KI
2500	1	$\log_{10}(\nu/\nu_0)$ stress, atm	0.00176 ——	0.00183 645	0.00232 846	0.00279 676	——
5000	1	$\log_{10}(\nu/\nu_0)$ stress, atm	0.00345 ——	0.00386 1371	0.00467 1550	0.00489 1516	0.00550 1176
7500	1	$\log_{10}(\nu/\nu_0)$ stress, atm	0.00431 ——	0.00564 2046	0.00623 2259	0.00689 2013	0.00702 1581
7500	24	$\log_{10}(\nu/\nu_0)$ stress, atm	0.00612 ——	0.00759 2989	0.00880 3012	——	——

40 % of the applied pressures.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—∇—∇—	7500	24	24

Fig. 9 F-bands in NaCl at about 23°C colored after compressing



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—∇—∇—	7500	24	24

Fig. 10 F-bands in KCl at about 11°C colored after compressing

Love[37] has derived the relationship between the positional coordinate of the particular element of the line and the radial displacement of the element from its equilibrium position. If the crystal is treated as an isotropic body, the positional coordinate of the particular element is equal to the crystallographic unit cell distance *a*, the radius of the external sphere of the crystal is infinite, the internal pressure is taken to be zero, and the external pressure is equal to the pressure p applied on the crystal, then the radial displacement U of the element derived from the relationship by Love is as follows:

$$U=-\left(\frac{1}{3k}+\frac{1}{4\mu}\right)pa,$$

where k is the bulk modulus, and μ is the shear modulus. The value of strain e defined as the fractional change of length, is

$$e=\frac{\partial U}{\partial a}=\left(1+\frac{3k}{4\mu}\right)+\left(\frac{1}{3k}+\frac{1}{4\mu}\right)p.$$

The bulk modulus and the shear modulus can be calculated from the following relationship derived by Wooster[38]

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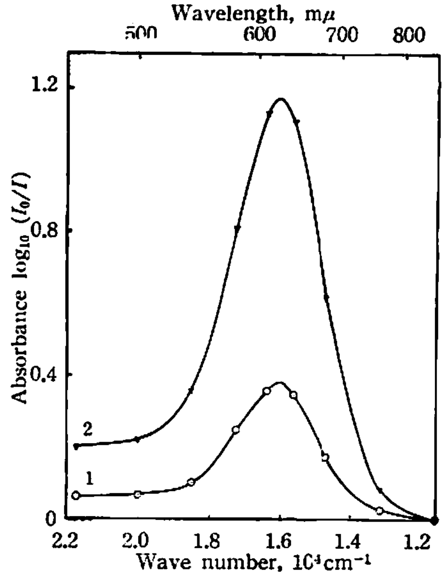
[37] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Cambridge Univ. Press, Cambridge, 1927) p. 142

[38] W. A. Wooster, *Crystal Physics* (Cambridge Univ. Press, Cambridge, 1937) p. 237



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—▽—▽—	7500	24	24

Fig. 11 F-bands in KBr at about 11°C colored after compressing

between a set of elastic coefficients, generally designated by C_{hk}, which have been determined experimentally by Huntigton[39], Galt[40], and Bridgman[41],

$$k = (C_{11} + 2C_{12})/3$$

$$\mu = C_{44} .$$

Not only the values of a, U, e, C_{hk}, k and μ, but also the negative of the slope of the experimental curves by Jacobs showing the dependence of the peak wave number on the lattice parameter, $-(\partial \ln \nu_m / \partial \ln a)_T$, and the experimental data of some elastic stiffness defined as the ratio between force and strain (Young's modulus, apparent elastic limit and modulus of rapture determined by Combes, Ballard and McCarthy[42], and the reciprocal of compressibility by Slater) are given in Table 5.

Table 5 The physical constants of alkali halides

Physical constants \ Crystals			LiF	NaCl	KCl	KBr	KI
Interionic distance	a	Å	2.01	2.81	3.14	3.29	3.53
Radial displacement	U ($p = 10^3$ atm)	Å	0.002	0.010	0.019	0.022	0.022
Strain	e ($p = 10^3$ atm)		1.80	2.45	3.08	3.22	2.8
$-(\partial \ln \nu_m / \partial \ln a)_T$			——	4.4	3.5	3.5	3.7
C_{hk} coefficient	C_{11}	10^{11} dyne/cm^2	9.77	4.85	3.98	3.45	3.32
	C_{12}	〃	4.04	1.23	0.62	0.540	0.578
	C_{44}	〃	5.55	1.26	0.625	0.508	0.620
Bulk modulus	k	〃	5.94	2.44	1.74	1.51	1.49
Shear modulus	μ	〃	5.54	1.26	0.625	0.508	0.620
Young's modulus		〃	7.0	4.0	3.0	2.7	——
Apparent elastic limit		10^7 dyne/cm^2	8.3	4.1	2.3	1.1	——
Modulus of rapture		〃	14.5	3.9	4.4	3.3	——
Reciprocal of compressibility		$\frac{1}{(1/v_0)(\partial v/\partial p)_T \times 10^6}$	$\frac{1}{1.53}$	$\frac{1}{4.18}$	$\frac{1}{5.65}$	$\frac{1}{6.68}$	$\frac{1}{8.56}$

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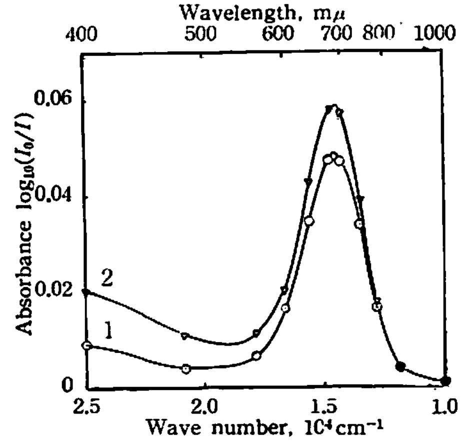
39) R. B. Huntington, *Phys. Rev.*, 72, 321 (1947)

40) J. K. Galt, *ibid.*, 73, 1460 (1948)

41) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 64, 305 (1929)

42) L. S. Combes, S. S. Ballard, and K. A. McCarthy, *J. Opt. Soc. Am.*, 41, 215 (1951)

The magnitude of the shifts of the peak wave numbers of the F-bands for the unit wave number, $\log_{10}(\nu/\nu_0)$ in Table 4, increases in the order of LiF $<$ NaCl $<$ KCl $<$ KBr $<$ KI, which coincides with the order of the interionic distance (a) and the radial displacement (U) at a certain pressures.



Curves No.	Legends	Pressures atm	Compressing hours	Hours from the end of the exposure to $RaBr_2$
1	—⊙—⊙—	1		24
2	—▽—▽—	7500	24	24

Fig. 12 F-bands in KI at about 22°C colored after compressing

The compounds showing the peaks of the F-bands at the longer wavelengths are more easily bleached. The rate of the spontaneous bleaching increases with increasing ionic distance which is proportional to the radius of the halogen-ion vacancy, in the order of LiF$<$NaCl$<$KCl$<$KBr$<$KI. The decrease of the spontaneous bleaching by the application of hydrostatic pressure may be ascribed to the decrease of the radius of the potential well of the halogen-ion vacancies, that is the increase of the dissociation energy between the F-center electron and the neighbouring alkali metal ions.

The concentration of the F-centers formed in the specimens by an exposure to $RaBr_2$ after compressing increases in comparison with that formed in the virgin specimens by an exposure at the same time. One of reasons of such enhancement of the concentrations of the F-centers by the application of hydrostatic pressure is decrease of the spontaneous bleaching by the residual strain in the specimens. Another reason of the enhancement of the concentration of the F-centers may be the increase of the density of the vacant lattice sites by the application of hydrostatic pressure. Nabarro[43] has explained about the creation of a vacant lattice site at the surface of a crystal under uniaxial homogeneous stress by the motion of the favorably situated atom. Seitz[23] has applied Nabarro's idea to the color center and indicated that the dislocations may act the sources or the sinks for the vacant lattice sites. Dexter[44] has calculated the interaction between the F-centers and the dislocations and shown that the F-centers located within about 50 A of edge-type dislocations would experience measurable broadening and perhaps shifting of their absorption peaks. Bridgman[45] has found that the internal slip without fracture occurs in brittle substance by simple tension or com-

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[43] F. R. N. Nabarro, *Report of a Conference of Strength of Solids* (The Physical Society, London, 1948) p. 75

[44] D. L. Dexter, *Phys. Rev.*, 93, 985 (1945)

[45] P. W. Bridgman, *J. App. Phys.*, 18, 246 (1947)

pression superposed to hydrostatic pressure. The F-bands after compressing show the broadening of the peaks to the short wavelengths, that is, the crystals have some magnitude of the residual strain still after releasing pressure. The residual strain is in the vicinity of the dislocations which are frozen at certain densities in the crystals, as Frank46), Verma47), and many other investigators have published about the role of the dislocations in the crystal growth, and it makes more easy the formation of the vacancies. Moreover, it would seem that a plastic flow on a local scale is caused at the surface of the crystals and in the vicinity of the dislocations by the application of hydrostatic pressure. The rate of enhancement of the concentration of the F-centers formed in the specimens after compressing increases in the order of $LiF < NaCl < KI < KCl < KBr$ with the increase of the strains at a certain pressure, e or $-(\partial \ln \nu_m / \partial \ln a)_T$, which is in accordance with the order of the decrease of the elastic stiffness except in the case of KI. The fact that the broadening of the peaks to the short wavelengths is found in the F-bands formed by the exposure to $RaBr_2$ within a certain duration (10 days for LiF) after compressing and not found over a certain duration indicates that the vacant lattice sites associated with the F-centers have been created during the crystal growth and the plastic flow on a local scale by the application of hydrostatic pressure.

The author has great pleasure in expressing his sincere thanks to his sponsor, Prof. R. Kiyama for his advice and encouragement throughout the course of this investigation. He is also indebted to the Department of Education for the Grant in Aid to the Researches by Junior Researchers in Research Institutions.

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46) F. C. Frank, *Disc. Farad. Soc.*, No. 5, *Crystal Growth*, 48 (1949)

47) A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, London, 1953) pp. 52~59