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A-Centers in Alkali Halide Crystals

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A review is given of recent experimental work on A-centers in KCl and KBr crystals doped with Li and Na. The time dependence of the optical absorption intensity during the formation, thermal destruction and thermal disorientation of A-centers is measured at various temperatures, and the corresponding activation energies are obtained. By analysing dichroic absorption spectra, the peak energies, half-widths and oscillator strengths of the A_1- and A_2-bands are determined. The photochemical conversion of A-centers into F-centers and A'-centers as well as the thermal destruction of A'-centers are also investigated, and A-centers in Li-doped crystals are found to be non-photoelectric below 30°C. Special attention is given to the optically induced reorientation of A-centers in KCl doped with Li, and the quantum efficiency of this process is measured as a function of temperature. Finally, mention is made of some interrelations with M-centers, and a new possible mechanism is suggested for the formation of A-centers.

Two absorption peaks called A_1 and A_2 have been observed in additively colored KCl crystals containing Na ions by irradiating with F-light near room temperature.[1)-4)] Both the A_1- and A_2-bands have been attributed to a common absorption center consisting of an F-center associated with a Na ion. This model was confirmed recently by an ENDOR experiment in KCl doped with Li.[2)]

The present paper reviews subsequent work which has been made in our laboratories on A-centers* in KCl and KBr doped with various kinds of foreign alkali ions.

1. General Properties

(1) *F→A transformation*

KCl and KBr single crystals doped with Li, Na, or Rb were grown by adding approximately 1 mole % of relevant halides to their melts. These crystals were additively colored as usual and quenched from about 500°C to room temperature within a time of 10~15 seconds. Under this condition, only the normal F-band appeared as in pure crystals. The initial concentrations of F-centers were of the order of 10^{17} per cm^3.

Our experimental results concerning optical bleaching of the F-band may be summarized as follows:

(a) With irradiating in the F-band at appropriate temperatures, the F-band decreases and the A-bands appear only when the radius of added foreign ions is smaller than that of a K^+ ion. Rb^+ ions do not affect photochemical properties of the crystals. In Table I are listed the peak energies and half-widths of the A-bands at −70°C determined by analysing their dichroic absorption spectra*.

Table I. Peak energies and half-widths of the A-bands measured at −70°C (in ev).

		KCl:Ki	KCl:Na	KBr:Li	KBr:Na
A_1	Peak	1.93	2.03	1.73	1.81
	Width	0.19	0.18	0.19	0.22
A_2	Peak	2.22	2.32	1.96	2.06
	Width	0.25	0.24	0.31	0.35
F	Peak	2.28		1.99	
	Width	0.28		0.30	

(b) The initial growth-rate of the A-bands in KCl:Na is nearly independent of temperature. In the other substances, however, the growth-rate becomes larger with increasing temperature so long as the temperature is

* A-centers are called F_A-centers by the Stuttgart School.

* The A-bands in KCl:Li is identified with the absorption bands noticed by Ishiguro and Sugioka.[6)]

not too high to be stable for A-centers. The activation energies for the $F \rightarrow A$ conversion obtained from these measurements are

KCl:Li	KBr:Li	KCl:Na	KBr:Na
0.18	0.20	0.0	0.27 (ev).

(c) F-centers disappear completely through the $F \rightarrow A$ conversion.

(d) During the $F \rightarrow A$ conversion, the total area under the absorption curve remains constant.

(e) The $F \rightarrow A$ conversion accompanies no measurable "incubation time" as has been observed[7] in the case of $F \rightarrow M$ transformation.

(2) *$A \rightarrow F$ conversion*

Li A-centers are photochemically stable at all temperatures below 30°C, whereas Na A-centers transform into F-centers by irradiating with A-light at temperatures where the $F \rightarrow A$ conversion is possible.

A-centers return to F-centers by warming the crystals in the dark. The speed of this conversion depends on substances. Fig. 1

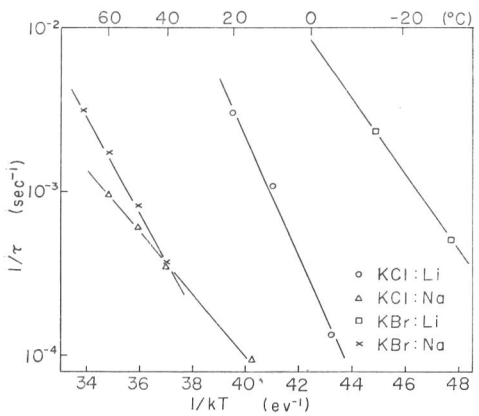

Fig. 1. Mean lifetime for the thermal destruction of A-centers measured at various temperatures.

shows the mean lifetime τ measured at various temperatures. From this figure we get as the activation energies for the thermal destruction:

KCl:Li	KBr:Li	KCl:Na	KBr:Na
0.84	1.05	0.43	1.06 (ev).

(3) *$A \rightarrow A'$ conversion*

When F-centers coexist with A-centers, the A-bands transform partially into a broad A'-band by irradiating in the F-band between −100°C and −150°C for KBr, and between −50°C and −110°C for KCl. A_1-light is also effective in the $A \rightarrow A'$ conversion for Na A-centers in the same temperature ranges even if there are no F-centers. The A'-center is now believed to be an F'-center associated with a foreign alkali ion.

On warming crystals containing A'-centers, the A'-band disappears and the crystals return to the conditions before the conversion. Whereas the Na A'-center is thermally a little more stable than the F'-center, the Li A'-center is less stable and its lifetime in KCl:Li, for example, is approximately 30 sec at −50°C.

(4) *Dichroism*

Dichroic absorption occurs when the A_1- or A_2-band is irradiated with ⟨100⟩-polarized light. The dichroism can be produced successfully at temperatures between 50°C and −70°C in KBr:Na, between −30°C and −70°C in KBr:Li, and at any temperatures below 0°C* in KCl:Li.

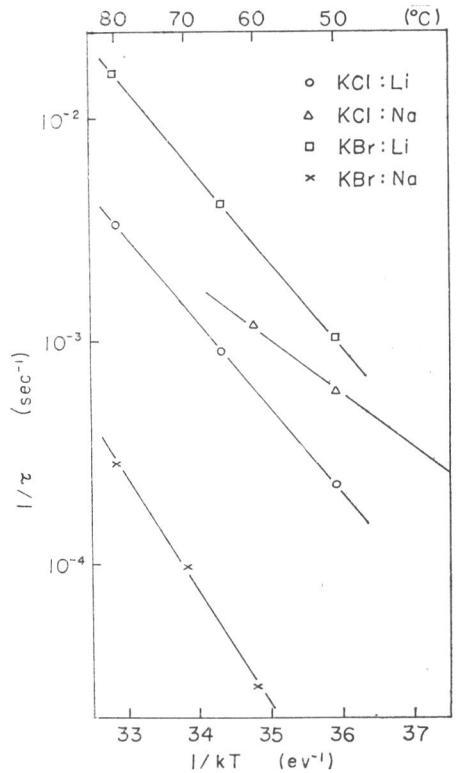

Fig. 2. Relaxation time for the thermal reorientation of A-centers measured at various temperatures.

* Ishiguro (private communication) has found the dichroism to appear even at liquid hydrogen temperature.

The dichroism disappears on warming the crystals as a result of thermal disorientation of A-centers. In Fig. 2 is plotted the relaxation time τ for this process against temperature T. The corresponding activation energies are

KCl:Li	KBr:Li	KCl:Na	KBr:Na
0.73	0.70	0.43	0.69 (ev).

It may be noticed that the thermal stability depends markedly on substances. Although in KCl:Na the disappearance of the dichroism takes place simultaneously with that of the A-bands themselves, this is not true for the other substances, *i.e.*, the former takes place more rapidly than the latter at any temperature.

(5) *Oscillator strength*

From analysis of dichroic spectra, we get values of oscillator strength of the A_1- and A_2-bands

$$f_1=0.90\pm0.02 \text{ and } f_2=0.83\pm0.02\,,$$

which are almost identical for the four substances. In obtaining these values, the shape of the bands is assumed to be symmetrical and the oscillator strength of the F-band is taken to be 0.85.

(6) *Relations to M-centers*

i) Na-doped crystals

Petroff[6] noticed that the growth of the M-band during F-band irradiation in KCl accompanies an "incubation time". We have examined this effect on both Na-doped and Na-free crystals and found that the growth-rate and hence the incubation time are nearly independent of their sodium content.

A-centers are gradually destroyed as M-centers are formed, which means that A-centers as well as F-centers contribute to the formation of M-centers.

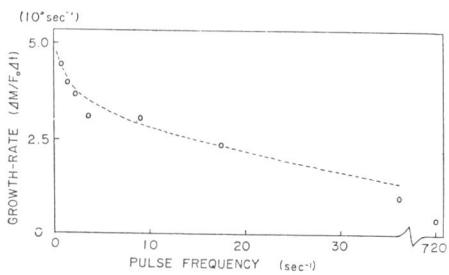

Fig. 3. Initial growth-rate of the M-band under pulsed F-light in KCl as a function of pulse frequency.

Under pulsed F-light (duration: 1/720 sec) with various periods (1~36/sec), it was observed that the growth-rate of A-centers is independent of the periods at any temperature, whereas that of M-centers depends unambiguously upon the periods as shown in Fig. 3.

ii) Li-doped crystals

Under prolonged F-band irradiation at room temperature, all F-centers are converted into A-centers and then no further changes occur in the absorption spectrum. This is in consistent with the fact that Li A-centers are non-photoelectric at this temperature.

2. Reorientation Rate of Optically Excited Li A-Centers

In general, dichroism appears at a given temperature only when the following three conditions are fulfilled at the same time:

i) The absorption centers with which we are concerned have lower symmetry than cubic.

ii) The centers are not free to make reorientation in its ground state in the dark.

iii) Either or both of the following processes occur: (a) The number of the centers decreases due to the production of photoelectrons. (b) Reorientation of the centers occurs as a result of optical excitation.

The dichroism in the Na A-bands produced by A_1- or A_2-light in a certain range of temperature is an example where both (a) and (b) are involved. On the other hand, the dichroism in the Li A-bands appearing at temperatures below 0°C and that in the Na A-bands produced near −180°C are examples where only the process (b) is involved.

The reorientation in KCl:Li may be particularly interesting since photoelectrons are not concerned in it, and moreover, it occurs over an exceedingly wide range of temperature. Therefore, a quantitative investigation of the reorientation rate was made on this substance. Let us now assume that a vacancy comprising an A-center makes a jump to one of its four other neighboring sites by exciting with [100]-polarized light with a probability β per absorbed quantum. During a short period of the irradiation Δt, the difference in the areas of the A_2-band as measured with [100]-polarized light and with [010]-polarized light is assumed to have changed

by ΔS. Then, by use of the Smakula's formula, we get expressions for $\Delta S/\Delta t$:

$$\left.\begin{aligned}\frac{\Delta S_1}{\Delta t} &= 6A\beta_1 f_1 \frac{q_1}{2}[1-\exp(-\alpha_1 l)] \\ \frac{\Delta S_2}{\Delta t} &= 3A\beta_2 f_2 \frac{q_2}{2}[1-\exp(-\alpha_2 l)]\end{aligned}\right\} \quad (1)$$

with

$$A=\frac{\pi e^2 h}{9mc}\frac{(n^2+2)^2}{n}\,.$$

In Eq. (1), the suffixes 1 and 2 refer to the A_1- and the A_2-bands respectively, and the other notations are as follows:

n: refractive index of the crystal,
l: thickness of the crystal,
q: number of incident photons per unit area and unit time,
α: absorption coefficient for the incident light.

Values of q were calibrated by making use of the $F\rightarrow F'$ conversion in a pure crystal. Substituting the observed values of ΔS in Eq. (1), we obtain

$$\beta_1=0.01\pm0.005$$

and

$$\beta_2=0.04\pm0.005\,,$$

which are approximately independent of temperature between $-30°C$ and $-180°C$.

These values are small indeed as compared with the value 1/4 which corresponds to an ideal case that the vacancy jumps by one step whenever the center is optically excited. However, they appear still appreciably large among various electron trapping centers which have shown dichroism by the mechanism (b).

In the case of KBr:Li corresponding quantitative measurements were rather difficult because the dichroism appears only in a relatively narrow temperature range ($-30°C$ $\sim-70°C$) but it was proved that the reorientation rate depends markedly on temperature unlike the case of KCl:Li.

3. Mechanism of Formation

Although a possible mechanism of the formation of A-centers was suggested in a previous paper[3], it appears necessary to modify some of the ideas presented in it. As noted there, the formation of an A-center must involve a transport of a halogen ion vacancy to the immediate vicinity of an impurity ion. When an optically excited F-center returns to its ground state or an electron is captured at a halogen ion vacancy, extra energy will be liberated to lattice vibration, causing a local heating around the F-center. This local heating will assist the migration of the F-center to combine with an isolated impurity ion.

One may be tempted to explain also the $F\rightarrow M$ conversion due to F-light in a similar fashion. But as mentioned before, the $F\rightarrow M$ conversion accompanies an incubation time while the $F\rightarrow A$ conversion does not. This seems to indicate that a basically different mechanism is involved in either of the two processes. This point should be explored further in future investigations.

A more detailed account of a part of this work will be published elsewhere.

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DISCUSSION

Pick, H.: What is the activation energy for A-center production in KCl(Na)?

At Stuttgart the production of A-centers in KCl(Na) was investigated (Haertel) using single shot light pulses. The conversion occurs in the dark, when F'-centers are destroyed. This means either the Na^+ or the F'-center moves. Activation energy is about 0.25 ev.

Kojima, T.: In KCl:Na, the production of A-centers apparently requires no activation energy, for their growth-rate is nearly temperature independent. Since this activation energy has been obtained under F-band illumination, it does not correspond to the actual formation energy of the A-center.