EPR and Optical Studies on γ-Ray Irradiated $CdCl_2$: Ag and $MgCl_2$: Ag

Hiroaki MATSUMOTO and Takeshi MIYANAGA*

Department of Physics, Faculty of Science, Kyoto University

Isothermal decay processes of two paramagnetic centers and one optical absorption band in γ-ray irradiated $CdCl_2$: Ag are investigated. Decay kinetics of these centers are observed as first order in the initial stage and second order in the latter stage. Activation energies of two paramagnetic centers A and B are 0.76 ev and 0.71 ev respectively for first order kinetics. In three optical absorption bands 397 mμ, 515 mμ and 1000 mμ, 397 mμ band is most sensitive for thermal treatments and activation energy of it is observed as 0.60 ev for first order kinetics and this band may correspond to either A or B center.

EPR and optical absorption spectra of γ-ray irradiated $MgCl_2$: Ag are also reported. Single C line at $g=2.034$, a broad band for Ag^{++} at $g=2.067$ and a pair of hyperfine lines of Ag^0 with $A/g\beta=1226$ G at $g=2.005$ are found in the EPR spectrum. Optical absorption spectrum is very similar to that of $CdCl_2$: Ag.

After consideration about thermal properties and correspondence of spectra of $CdCl_2$: Ag and $MgCl_2$: Ag, it is proposed that models for B and C centers are tetrahedrally arranged aggregate of Cd^{++} ions with an unpaired electron and similar aggregate of Mg^{++} ions with an unpaired hole respectively.

I. INTRODUCTION

In the previous paper,[1] it was reported that two paramagnetic centers (A and B centers) were found in the γ-irradiated $CdCl_2$: Ag crystal. Proposed models for these centers were as follows : that is, one is Ag^{++} center (A center) accompanied with a Cl^- ion vacancy at the nearest neighbour site and the ground state is $^2E\theta$, the other (B center) is the aggregate composed of tetrahedrally arranged metal ions which capture an extra electron with it. It was not evident at that time whether the metal ions are doped silver or cadmium of host crystal in the model of B center.

Thermal stabilities of EPR and optical absorption spectra of γ-irradiated $CdCl_2$: Ag have been studied and further EPR and optical absorption spectra of γ-irradiated $MgCl_2$: Ag have been studied to confirm these models and to make clear the mutual interaction of these centers.

In this report, optical absorption spectra of γ-irradiated $CdCl_2$: Ag and $MgCl_2$: Ag are described. And a study on thermal decay of EPR and optical absorption spectra of γ-irradiated $CdCl_2$: Ag is developed and some results concerning with the decay kinetics and electron or hole nature of paramagnetic centers and cor-

---

* 松本　弘明，宮永　健史

respondence of 400 mμ (397 mμ) optical absorption to EPR centers are given.

Moreover, EPR spectrum of γ-irradiated MgCl$_2$: Ag is described and properties of three kinds of absorption lines are discussed. One of which corresponds to B lines of CdCl$_2$: Ag and it leads to the conclusion that the metal aggregates of B and C centers are that of host crystal and not silver ions and further another one of which corresponds to Ag^0 which has anomalously large hyperfine splitting.

II. EXPERIMENTAL PROCEDURES

II. 1. Sample Preparation

CdCl$_2$: Ag and MgCl$_2$: Ag crystals were grown with the same technique as was described earlier.[1] Since MgCl$_2$ was partially resolved during evacuation and drying and excess metal were precipitated at the lower part of the crucible, pull down method such as Stockbarger-method was not suitable for obtaining good samples.

γ-ray irradiation was made on the samples kept in evacuated glass tube at room temperature in the Co^{60} furnace with a facility of the Institute for Chemical Research of Kyoto University.

γ-ray dose was about $7\sim15\times10^6$ r.

II. 2. EPR and Optical Absorption Measurements

Measurements of EPR spectra were done with the use of usual type K-band spectrometer at room or liquid nitrogen temperatures.

Isothermal decay curves of EPR absorptions were obtained by repeating following procedures: samples were heated for a certain minutes in the furnace which was kept at a definite temperature and then changes of absorption intensities between before and after this heat treatment were measured at room temperature. A definite amount of DPPH was used as the intensity standard for the intensity measurements of EPR.

Optical absorption measurements were made at room or liquid nitrogen temperatures with *Shimadzu MPS 50 L* type recording spectrophotometer. Direction of incident light was parallel to the crystal c-axis.

Isothermal decay curves of optical absorptions were obtained as the same method as that of EPR.

Since CdCl$_2$ is very hygroscopic, samples were covered with polystyrene film during these heat treatments and measurements. Polystyrene film does not make any disturbance for measurements because it is transparent for the region between 300 mμ and 2000 mμ and stable for the temperature range between room temperature and 140°C. MgCl$_2$: Ag is more hygroscopic than CdCl$_2$: Ag, but polystyrene film was not used for the absorption measurement of MgCl$_2$: Ag because this has optical absorption bands at the shorter wave length side of 300 mμ where polystyrene has intense absorption. Careful treatments were needed to avoid the effect of moisture for measurement of the absorption spectra of MgCl$_2$: Ag.

III. RESULTS

III. 1. Optical Absorption Spectra of CdCl$_2$: Ag

Pure CdCl$_2$ has the threshold of fundamental absorption at about 230 mμ and has not any dominant absorption band up to 2000 mμ at the longer wave length side of it.[2,3] γ-ray irradiation at room temperature did not cause any absorption change in this range for CdCl$_2$.

CdCl$_2$: Ag did not show any absorption band between 250 mμ and 2000 mμ as same as pure CdCl$_2$ but γ-irradiation at room temperature produced three absorption bands at 397 mμ, 515 mμ and 1000 mμ for CdCl$_2$: Ag.

Absorption spectra of CdCl$_2$: Ag are shown in Fig. 1, curve (a) is a spectrum before irradiation with γ-ray, measured at liquid nitrogen temperature, curve (b) is a spectrum after irradiation with γ-ray, measured at liquid nitrogen temperature and cuve (c) is a spectrum after γ-irradiation measured at room temperature.
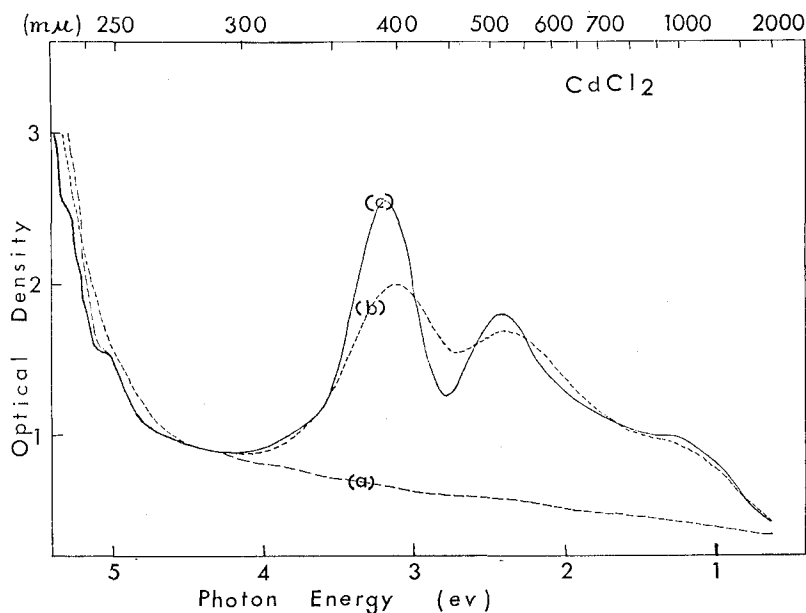

Fig. 1. Optical absorption spectra of CdCl$_2$: Ag.
Curve (a) is a spectrum before irradiation with γ-ray, measured at liquid nitrogen temperature, curve (b) is a spectrum after irradiation with γ-ray, measured at room temperature, curve (c) is a spectrum after γ-irradiation measured at liquid nitrogen temperature.

397 mμ and 515 mμ bands become sharper at lower temperature and 397 mμ band at room temperature makes shift its peak to shorter wave length side 390 mμ at liquid nitrogen temperature. Total intensities of each bands do not change with temperature. Since 245 mμ and 234 mμ peaks observed at liquid nitrogen temperature were very difficult to make sure the reproducibility in each measurement, they are put aside from consideration in this report.

III. 2. Thermal Stability of γ-irradiated CdCl₂ : Ag
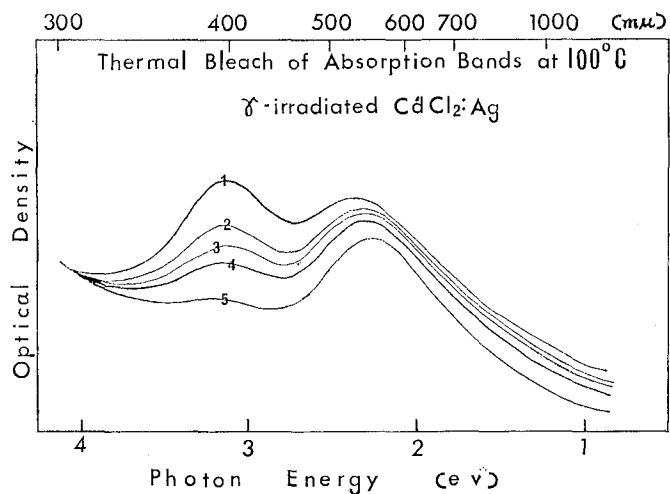
Measurements of thermal decay for both EPR and optical absorption bands

Fig. 2. Isothermal decay of optical absorption spectra of γ-irradiated CdCl₂ : Ag.
Heat treatments are made at 100°C and absorption measurements are made at room temperature. Curve 1: spectrum before heat treatment, curve 2: heat treated for 4 minutes, curve 3: heated for 6 minutes, curve 4: heat treated for 8 minutes and curve 5: heat treated for 13 minutes.
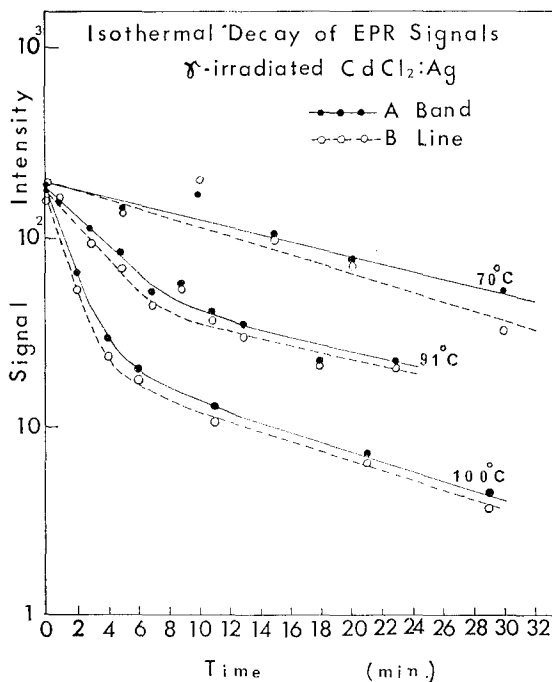

Fig. 3. Isothermal decay of A band and B lines in EPR spectra of γ-irradiated CdCl₂ : Ag.
Heat treatments are made at 70°C, 90°C and 100°C. Solid lines are for A band and dashed lines are for B lines. Intensity measurements are made at room temperature and a finite amount of DPPH is used for an intensity standard.
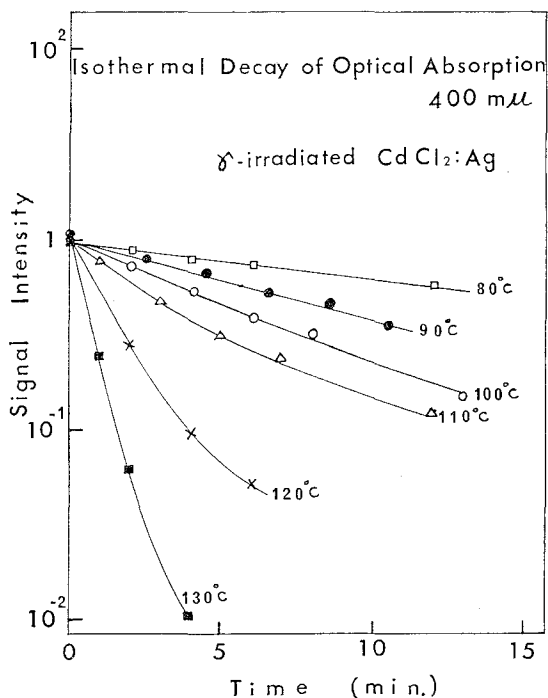
Fig. 4. Isothermal decay of 400 mμ band (397 mμ) in optical absorption spectra of γ-irradiated CdCl₂ : Ag.
Temperatures of heat treatments are 80°C, 90°C, 100°C, 110°C, 120°C and 130°C. Absorption measurements are made at room temperature.

were made to see the stabilities and mutual interactions of paramagnetic centers and further to see whether an optical absorption band can correspond to any paramagnetic centers.

Isothermal decay of optical absorption spectra at 100°C are shown in Fig. 2., curve 1 shows the spectrum which did not suffer any heat treatments, curve 2 : heat treated for 4 minutes, curve 3 : heat treated for 6 minutes, curve 4 : heat treated for 8 minutes, and curve 5 : heat treated for 13 minutes. Decay of 400 mμ band is dominant.

Isothermal decay curves of EPR signals and optical 400 mμ band with respect to heating time are given in Fig. 3 and Fig. 4. It become clear that the isothermal decay of A band is almost parallel to that of B lines, this means that B center is a complementary one of A center. Since A center is a hole center (Ag^{++})[1], B center must be a center which captures an excess electron.

If the thermal decay process is governed by first order kinetics, concentration of center is given as a function of temperature and time as following :

$$n = a \exp\{-s_1\, t\, e^{-E/kT}\} \tag{1}$$

where n : concentration of center, E : activation energy of thermal decay, s : frequency factor of thermal decay, a : constant, T : temerature in °K, t : time, k : Boltzmann's constant. Initial decrease in isothermal decay curves of EPR and

optical $400\,\mathrm{m}\mu$ band in Fig. 3 and Fig. 4 shows considerablly good fit in Eq. (1). This means that the first stage of isothermal decay processes of A center, B center and optical $400\,\mathrm{m}\mu$ band follows first order kinetics.

Latter part of decay curves may be governed by other kinetics. In general i-th order kinetics $(i\neq1)$ gives the concentration of centers with Eq. (2):

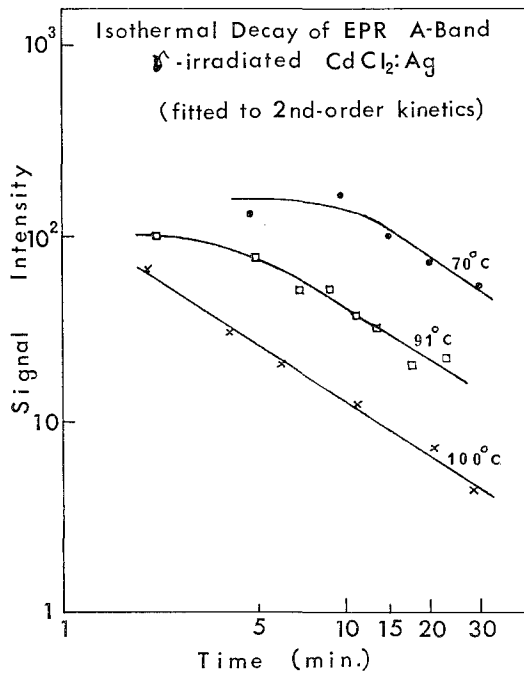$$n^{(1-i)} = (i-1)s_i\,t\,\exp\,(-E/kT) \qquad (2)$$

Fig. 5. ln n vs ln t is plotted for the isothermal decay of A band.
Where n is intensity of A band and t is heat treating time. Straight line parts of curves can be fitted in the second order kinetics.
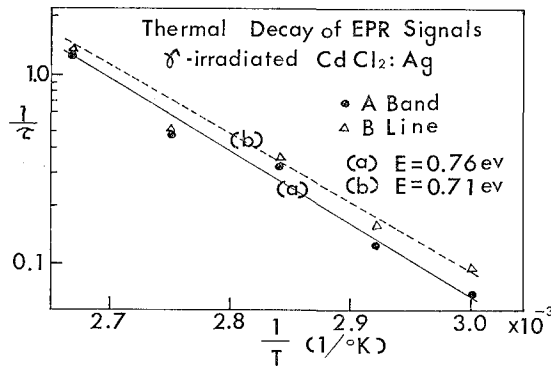

Fig. 6. Gradients of isothermal decay curves in their initial stages as a function of inverse temperatures for EPR signals of γ-irradiated CdCl$_2$: Ag.
Activation energies are obtained as gradients of these lines. (a) is for A band, activation energy of A band is 0.76 ev. (b) is for B lines, activation energy of B lines is 0.71 ev.
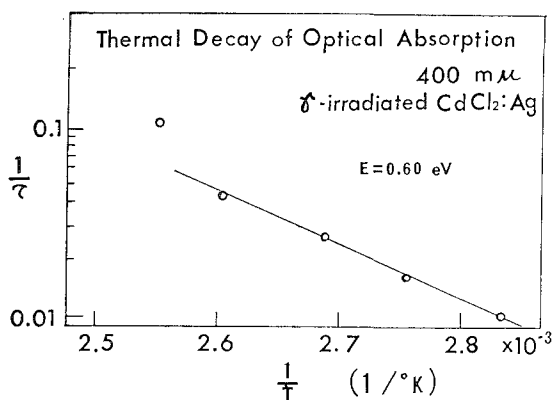
Fig. 7. Gradients of isothermal decay curves in their initial stages as a function of inverse temperatures for 400 mμ optical absorption band of γ-irradiated CdCl$_2$: Ag. Activation energy is 0.60 ev.

Eq. (2) shows that graph for $\ln n$ vs $\ln t$ becomes a straight line with a gradient of $1/(1-i)$ in the case of i-th order kinetics. $\ln n$ vs $\ln t$ is poltted for EPR A band in Fig. 5, latter part of these curves can be fitted in Eq. (2) with $i=2$.

It may be concluded that isothermal decay of A center and also B center follows second order kinetics in the latter stage.

Thermal activation energies are also obtained for A center, B center and 400 mμ band by plotting the gradients of first order kinetics parts of decay curves with respect to inverse temperature $1/T$. This is done in Fig. 6 ((a) : A band and (b) : B band) and Fig. 7 (400 mμ band), where $1/\tau$ is gradient of decay curve (Fig. 3 and Fig. 4) and τ corresponds to relaxation time of center.

Obtained values of activation energiy for first order kinetics are as follows :
$E=0.76$ ev for A band, $E=0.71$ ev for B lines and
$E=0.60$ ev for optical 400 mμ band.

Other bands in the optical absorption spectra were stable at 140°C or higher temperature. The most stable one was 1000 mμ band.

III. 3. Optical Absorption and EPR of γ-irradiated MgCl$_2$: Ag

(a) Optical Absorption

It has been reported that MgCl$_2$ has the threshold of fundamental absorption at about 160 mμ,[3,4] but in our measurement on undoped MgCl$_2$ crystal strong absorption began to rise at about 240 mμ and absorption change in shorter wave length side caused by doped Ag or γ-ray irradiation could not be measured.

γ-ray irradiation on MgCl$_2$: Ag produced three absorption bands 265 mμ, 345 mμ and 455 mμ as shown in Fig. 8. Absorption measurement at liquid nitrogen temerature revealed that 455 mμ band is composed with two bands at 440 mμ and 480 mμ. In Fig. 8, curve (a) shows undoped MgCl$_2$ without γ-ray irradiation measured at room temperature, curve (b) : MgCl$_2$: Ag without γ-ray irradiation measured at room temperature, curve (c) : γ-ray irradiated MgCl$_2$: Ag measured at room temperature, curve (d) : γ-ray irradiated MgCl$_2$: Ag measured at liquid nitrogen temperature.
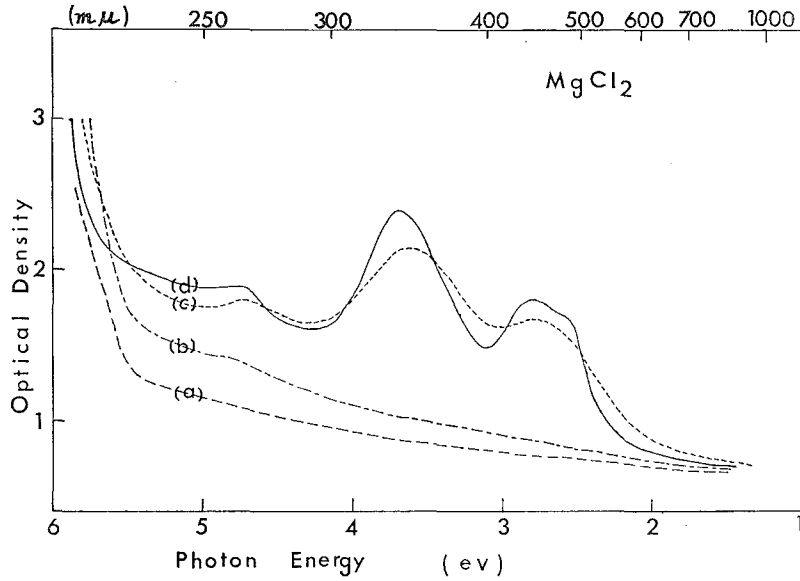
(49)

Fig. 8. Optical absorption spectra of MgCl₂ and MgCl₂ : Ag. Curve (a) is a spectrum of undoped MgCl₂ measured at room temperature, curve (b) is a spectrum of MgCl₂: Ag before γ-irradiation, curve (c) is a spectrum of γ-irradiated MgCl₂ : Ag measured at room temperature and curve (d) is a spectrum of γ-irradiated MgCl₂ : Ag measured at liquid nitrogen temperature.

Through the intensity ratios of 265 mμ band to other bands differed from sample to sample, the intensity ratio between 345 mμ, 440 mμ and 480 mμ bands were kept constant in any samples. All bands were stable to about 150°C.

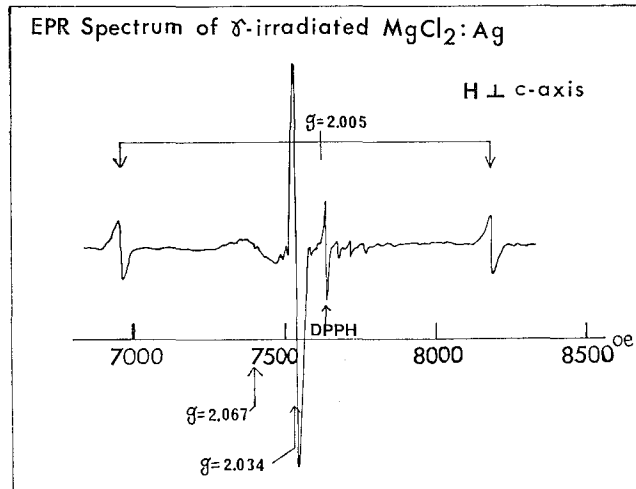**(b) EPR of γ-irradiated MgCl₂ : Ag**

Fig. 9. EPR spectra of γ-irradiated MgCl₂ : Ag measured at liquid nitrogen temperature.
Three kinds of signals at $g=2.034$, $g=2.005$ and $g=2.067$ are observed. DPPH is used as a marker of $g=2.0036$.

Three kinds of EPR absorption bands were observed in γ-irradiated MgCl₂ : Ag. They were very faint at room temperature but very prominent at liquid nitrogen temperature. EPR spectra measured at liquid nitrogen temperature is shown in Fig. 9, direction of static magnetic field is perpendicular to crystal *c*-axis.

Spectra are composed of following three kinds of bands.

(i)　Single line at $g=2.034$ is most intense band and peak to peak width is about 30 oe. This line can be considered to correspond to B lines of γ-irradiated CdCl₂ : Ag and due to an aggregate of metal ions of host crystal as will be discussed later. This line is designated as C line tentatively.

(ii)　A pair of sharp lines which appears at both ends of the spectra is considered to be hyperfine lines of neutral silver. The intensity ratio of these lines to C line varies from sample to sample. Hamiltonian for these lines is as follows :

$$H = g\beta H\,\mathrm{M} + A\,\mathrm{m}\,\mathrm{M} + \frac{A^2}{2g\beta H}[-\mathrm{m}\{\mathrm{S(S+1)} - \mathrm{M}\} + \mathrm{M}\{\mathrm{I(I+1)} - \mathrm{m}^2\}] \quad (3)$$

where H : static magnetic field, β : Bohr's magneton, S : electron spin quantum number, M : electron spin magnetic quantum number, I : nuclear spin quantum number, m : nuclear spin magnetic quantum number, A : hyperfine constant ; S = 1/2, M = ±1/2, I = 1/2, m = ±1/2 for neutral silver. Transitions are allowed for $\Delta\mathrm{M} = \pm1$, $\Delta\mathrm{m} = 0$. Values of g and A are $g = 2.005$ and $A = 1146 \times 10^{-4}$ cm⁻¹ (1226 Gauss).

The ground state of neutral silver is ²S and its electronic configuration is $(4s)^2$ $(4p)^6$ $(4d)^{10}$ $(5s)^1$. Then the values of g is expected to be nearly equal to the free g value 2.0023 but in our case a positive g-shift $\Delta g \approx 0.003$ is obtained. While hyperfine splitting constants of free atoms are 612.5 G (¹⁰⁷Ag) and 707.3 G (¹⁰⁹Ag) and that of neutral silver in KCl crystal is 649 G, our value is much larger than them and nearly twice as large.

(iii)　A broad band at $g = 2.067$ has a peak to peak width of about 100 oe. This band corresponds to the A band of CdCl₂ : Ag and due to Ag⁺⁺ ion in the crystal. The intensity of this band is so weak that it could not be observed in some samples.

In addition to these three kinds of bands weak signals due to Mn⁺⁺ ions contained as an inpurity in MgCl₂ are appeared in the spectra.

IV.　DISCUSSION

IV.　1.　Thermal Stability of γ-irradiated CdCl₂ : Ag

As an A center is a hole center composed of an Ag⁺⁺ ion and a negative ion vacancy at a nearest site of it,[1] the parallel thermal decay of A and B centers in CdCl₂ : Ag will lead to the conclusion that a B center is an electron excess paramagnetic center.

Number of A center is considerablly larger than that of B centers because the total intensity of A band is far larger than that of B lines in the EPR spec-

trum of γ-irradiated $CdCl_2$: Ag. Then the thermal decay of A band may govern the thermal decay processes, in other words holes thermally released from A centers may induce the destruction of A centers and B centers.

Thermal decay kinetics can be treated at the same standing points of view as the study of thermoluminescence phenomena. Then behaviours of hole released from A center is considered to be in the three ways as follows :

(a) Recombination with an electron trapped at B center.

(b) Being captured by unfilled hole trap like as Cd^{++} ion vacancy.

(c) Being retrapped by A center.

Assuming these behaviours of hole and that the rate of processes (a) to (b) is constant throughout the decay process, isothermal decay rate of centers is given in Eq. (4) as following :[5,6]

$$-\frac{dn}{dt} = \frac{A_n \, m \, n \, s \, e^{-E/kT}}{\alpha A_n n + A_m (N-m)} \qquad (4)$$

where m : number of filled A centers, $N-m$: number of vacant A centers, n : number of filled B centers, A_n : probability of hole electron recombination, α : proportional constant, A_m : probability of retrapping of hole by vacant A center and $s \, e^{-E/kT}$: probability of thermal release of hole from A center at temperature T.

If we assume $A_m(M-m) \ll \alpha A_n n$ and $m \propto n$ in Eq. (4),

$$-\frac{dn}{dt} = n \, s_1 \, \exp(-E/kT) \qquad (5)$$

is obtained. Eq. (5) can be solved to give Eq. (1) of first order kinetics which shows good agreement with initial stage isothermal decays of A, B centers and 400 mμ band. This means that in the initial stage of isothermal decay majority part of holes from A centers will recombine with electrons at B centers or will be captured by hole centers such as Cd^{++} ion vacancies and retrapping process by vacant A centers will be negligible.

If $A_m(N-m) \gg \alpha A_n n$ and $N-m$ is nearly constant in Eq. (4),

$$-\frac{dn}{dt} = n^2 \, s_2 \, \exp(-E/kT) \qquad (6)$$

is obtained. This leads to the formula of second order kinetics Eq. (2) where $i=2$ and can be fitted in latter stages of isothermal decay experiments. This means that the retrapping process of released holes by vacant A centers is dominant in the latter stage of isothermal decay.

Though activation energies of A (0.76 ev) and B (0.71 ev) centers are somewhat larger than that of 400 mμ optical absorption band (0.60 ev), decay kinetics and decay temperatures are very similar for both cases and it will be natural to conclude that either of A or B center can correspond to 400 mμ optical absorption band. It would be necessary to investigate anisotrpic properties of 400 mμ band to know which center of A or B can be responsible to 400 mμ band because A center is anisotropic but B center is isotropic as was described in the previous paper[1].

IV. 2. EPR Spectrum of γ-irradiated MgCl₂ : Ag

(i) C line

C line at $g=2.034$ in Fig. 9 corresponds to B lines in the EPR spectrum of γ-irradiated CdCl₂ : Ag. Though B lines are composed of about five lines, C line is a single one. This difference suggests that B and C lines are not responsible directly to Ag or Cl which are common to both crystals and that they are responsible to Cd and Mg respectively. Two possible models were proposed for B lines of CdCl₂ : Ag in the previous paper,[1] one of these models, aggregate of Ag^+ ions with an electron, can be eliminated at this stage, another model, tetrahedral aggregate of Cd^{++} ions with an electron, can be supported for B lines. In the case of MgCl₂ : Ag, aggregate of Mg^{++} ions can compose the C center and this model leads to a single lines in EPR spectrum because nuclear magnetic moments of ^{24}Mg (78.6 % abundance) and ^{26}Mg (11.3 % abundance) are zero ($I=0$) and ^{25}Mg of $I=5/2$ has only 10.1 % of natural abundance and many lines owing to appearance of ^{25}Mg in the aggregate will be so weak in intensities that they will not be observed.

B center of CdCl₂ : Ag is concluded to be an electron center as is described earlier, but C center of MgCl₂ : Ag is considered to be rather a center with a hole because electron center Ag^0 is dominant in the case of γ-irradiated MgCl₂ : Ag, which does not appear in the case of γ-irradiated CdCl₂ : Ag and further broad band owe to Ag^{++} is very much weaker in the case of the former than that in the latter. Positive g-shift $\varDelta g \approx 0.032$ also supports that C center is a hole center.

As a suitable model of C center, we can propose a center composed of an aggregate of Mg^{++} ions and a hole which has been produced by γ-ray irradiation and has been captured by the aggregate.

(ii) Neutral Ag

Observed value of hyperfine splitting $A/g\beta=1226G$ is too much larger than that of free silver atom. This cannot be explained by considering only an electronic configuration $(4s)^2 (4p)^6 (4d)^{10} (5s)^1$ for the ground state of the neutral silver in MgCl₂ crystal. Neutral silver must suffer comparablly strong modification in its electronic configuration by the effect of ligand ions. Electronic configuration $(4s)^1 (4p)^6 (4d)^{10} (5s)^2$ may be mixed to the ground state of neutral silver in this case. This may increase hyperfine splitting because unpaired $4s$ electron has larger distribution at the position of nucleus of silver than $5s$ electron does and this contributes to increase Fermi term of hyperfine interaction.

Since the hyperfine splitting is very large, it is necessary to take second order contribution of hyperfine splitting into the determination of g-value. Obtained value of g is 2.005 and a positive g-shift $\varDelta g \approx 0.003$ is recognized. This g-shift may be able to be explained by considering the partial transfer of electron from ligand Cl⁻ ions into silver atom according to the theory which Watanabe has developed.[7] However the effect of partial electron transfer on hyperfine splitting may have an inclination to decrease it. Detailed consideration and estimation are necessary to explain the large hyperfine splitting and positive g-shift without any contradiction.

(iii)   Ag^{++} center

It was not successful to recognize anisotropy and resolution of Ag^{++} band at $g=2.067$ because the signal was too weak.   In γ-irradiated MgCl$_2$: Ag, aggregates of Mg^{++} may act as hole traps and Ag$^+$ ions may act as stronger traps for electrons than for holes, MgCl$_2$: Ag differs from CdCl$_2$: Ag in these points.

Sufficient information about a role of Mn^{++} ion contained in MgCl$_2$: Ag during γ-ray irradiation has not been obtained.

V. CONCLUSION

It is concluded that decay of A centers governs the isothermal decay process of B centers in γ-ray irradiated CdCl$_2$: Ag and B center is a paramagnetic center composed of tetrahedrally arranged Cd^{++} ions of host crystal and an electron trapped in this metal aggregate.

It is also determined that isothermal decay of A, B centers and 400 mμ band in CdCl$_2$: Ag follows to the first order kinetics at initial stage and second order kinetics at latter stage of decay.

Either of A band or B lines in EPR spectra may correspond to 400 mμ band in optical absorption spectra of γ-irradiated CdCl$_2$: Ag.

Dominant neutral silver center and a center of Mg^{++} aggregate with a hole are produced in MgCl$_2$: Ag by γ-ray irradiation.   Small amount of Ag^{++} centers are also produced in MgCl$_2$: Ag by γ-ray irradiation.

VI. ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Professor Y. Uchida and Professor K. Fukuda for the continuous guidance and encouragement throughout the work.   They are also indepted to Dr. K. Nakamura for the helpful discussions. Their thanks are also due to Professor S. Shimizu and to R. Katano for extending the facilities for γ-ray irradiation to their work.

REFERENCES

(1)   H. Matsumoto and T. Miyanaga, *Bull. Inst. Chem. Res. Kyoto Univ.*, **44**, 1 (1966).
(2)   H. Fesefeldt, *Z. Physik,* **64**, 741 (1930).
(3)   Makoto Watanabe and Hiroshi Yamashita (private communication).
(4)   E. G. Schneider and H. M. O'Brian, *Phys. Rev.*, **51**, 293 (1937).
(5)   A. Halperin and A. A. Braner, *Phys. Rev.*, **117**, 408 (1960).
(6)   C. E. May and J. A. Partridge, *J. Chem. Phys.*, **40**, 1401 (1964).
(7)   H. Watanabe, *Phys. Rev.*, **149**, 402 (1966).