

Electron Paramagnetic Resonance Studies on γ -Ray Irradiated $\text{CdCl}_2:\text{Ag}$ and $\text{CdCl}_2:\text{Cu}$ Crystals

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The electron paramagnetic resonance spectrum of γ -ray irradiated CdCl_2 doped with AgCl or CuCl is studied. γ -ray irradiation is made with Co^{60} at room temperature. Irradiation dose is about 15×10^{16} r. Two paramagnetic centers are found in irradiated $\text{CdCl}_2:\text{Ag}$. One is substitutional Ag^{++} ion associated with Cl^- ion vacancy. The values of g tensors for this center are $g_{ww}^2 + g_{uu}^2 = 4.4184$, $g_{uu}^2 + g_{ww}^2 = 4.2929$, $g_{vv}^2 = 4.2860$ and g_{uv} ($g_{vw} + g_{wu}$) $= 0.3459$, values of hyperfine constants are $\frac{|A_c^{Ag}|}{g\beta} = \frac{|A_c^{Cl}|}{g\beta} = 30$ gauss. The other center may be an electron trapped by tetrahedral aggregate of Ag^+ ions or Cd^{++} ions. ERP pattern is observed at $g=2.014$ and consists of five lines with a intensity ratio 1:5:10:5:1. In irradiated $\text{CdCl}_2:\text{Cu}$, it is found that substitutional cupric ion is responsible to ERP and the values of g tensors and hyperfine constants are $g_{ww}^2 + g_{uu}^2 = 4.783$, $g_{uu}^2 + g_{ww}^2 = 4.987$, $g_{vv} = 2.362$, g_{uv} ($g_{vw} + g_{wu}$) $= 0.759$ and $\frac{|A|}{g\beta} = 110$ gauss. Elongated tetragonal deformation on octahedral environment is concluded.

I. INTRODUCTION

Ag or Cu atom has the electronic configurations $(4d)^{10} (5s)^1$ or $(3d)^{10} (4s)^1$ respectively and they can remain as stable impurities in states of doubly charged positive ions, singly charged positive ions or neutral atoms in various crystals. When Ag or Cu are doped in CdCl_2 crystals as AgCl or CuCl , they may disperse in the host crystals as Ag^+ or Cu^+ ions with the electronic configuration $(4d)^{10}$ or $(3d)^{10}$ respectively and show no electron paramagnetism. However, an irradiation on these crystals with ionizing radiation such as γ rays or x rays changes the valence of Ag^+ or Cu^+ impurities and these ions would come to have unpaired electrons.¹⁾ Further, a certain mutual interaction between Cd^{++} $(4d)^{10}$ ions and Ag^+ $(4d)^{10}$ ions may occur through an action of unpaired electron under the irradiation of ionizing radiation in these crystals. These phenomena may be able to be investigated with the use of electron paramagnetic resonance.²⁾

One of the authors³⁾ has investigated the EPR of cupric ions in CdCl_2 doped as doubly charged ions and has found that cupric ions occupy substitutional metal ion sites and suffer a tetragonally deformed octahedral field and trigonal field in the direction parallel to crystal c -axis and their orbital doublet ground states 2E_g are split into orbital singlets with the action of tetragonal deformation. EPR absorption near $g \approx 2$ as we observed is only expected for the orbital singlet ground state. The irradiation induced Ag^{++} , Cu^{++} or Cd^{+++} ion has the same ground state 2E_g

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in octahedral field and tetragonal deformation is also needed to split the orbital degeneracy.⁴⁾ In the case of the irradiation induced paramagnetic impurities, imperfections such as chlorine ion vacancies may be able to contribute to make octahedral environments to deform tetragonally.

In this, paper, it is attempted to report the results of EPR investigations on the γ -ray irradiation induced centers in CdCl_2 doped with AgCl or CuCl .

II. EXPERIMENTS

II. 1. Sample Preparation

$\text{CdCl}_2:\text{Ag}$ or $\text{CdCl}_2:\text{Cu}$ crystals were grown from melt of CdCl_2 containing about 1~0.5 mole percent of AgCl or CuCl respectively in the evacuated quartz tube or glass tube. Since crystals are very hygroscopic, γ -ray irradiation was made on the samples kept in evacuated glass tube. γ -ray dose was about $15 \times 10^6 \text{r}$ and irradiation was made at room temperature in the Co^{60} facility of the Institute for Chemical Research of Kyoto University.

γ -ray irradiated samples were coloured dark blue black ($\text{CdCl}_2:\text{Ag}$) or green blue ($\text{CdCl}_2:\text{Cu}$), but they bleach within few ten hours at room temperature. EPR measurements were made on the coloured samples.

II. 2. EPR Measurements of $\text{CdCl}_2:\text{Ag}$

In EPR measurements, x-band microwave was used at liquid air temperature and k-band microwave was used for measurements at -100°C . The results are shown in Figs. 1 (a), (b) and 2, two kinds of signals are found: (A) broad and anisotropic bands which appear in lower magnetic field $g=2.167\sim 2.005$. We designate these bands as Ag-A bands tentatively, (B) five sharp lines centered at 3335 gauss (x-band) or 8622 gauss (k-band), line distances are about 22 gauss and isotropic, we call these lines as Ag-B lines.

(A) **Ag-A bands.** These bands are composed of broad bands and few resolved lines. In Fig. 3, anisotropy of EPR pattern measured with x-band microwave is shown, static magnetic field was rotated in the plane containing crystal c -axis and

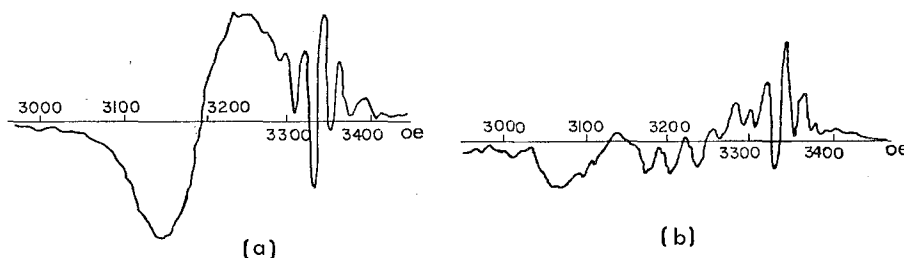


Fig. 1. Electron paramagnetic resonance spectra of γ -ray irradiated $\text{CdCl}_2:\text{Ag}$ crystal. Measurement is made at liquid air temperature and x-band microwave is used. Direction of static magnetic field is
 (a) parallel to the crystal c -axis,
 (b) $\theta=150^\circ$, $\phi=72^\circ$, where θ denotes angle between static magnetic field and crystal c -axis, ϕ angle between u -axis (see Fig. 5) and projection of static magnetic field on u - v plane.

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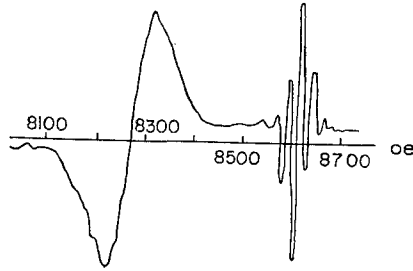


Fig. 2. Electron paramagnetic resonance spectra of γ -irradiated $\text{CdCl}_2:\text{Ag}$ crystal. Measurement is made at -100°C and k-band microwave is used. Direction of static magnetic field: $\theta=90$.

$\phi=72^\circ$ (see Fig. 5). The points marked with \times show positions of resolved lines in Ag-A bands and vertical lines show positions of broad bands and their lengths show the peak-to-peak widths of bands.

As will be discussed later in Chapt. III, Ag-A band is due to the substitutional Ag^{++} ion. A Cartesian coordinate system is defined such that the origin is placed at the Ag^{++} site and x, y and z axes are parallel to the axes extending from the origin to the properly chosen three Cl^- ions among the octahedral environment (Fig. 5). Three possible tetragonal axes exist, *i. e.*, x, y and z axes. When we assume that one of the six chlorine ions of octahedral environment is vacant and the octahedral environment deforms tetragonally owing to this vacancy, then the ground orbital doublet 2E_g of Ag^{++} splits into orbital singlets ${}^2E_\theta$ and ${}^2E_\epsilon$. This assumption is affirmed by the observed hyperfine structure of Ag^{++} ion and one Cl^- ion, as is described later. Accordingly EPR spectra show three overlapping patterns for a direction of static magnetic field, each corresponds to x, y and z tetragonal deformation axes respectively. Broad bands in Figs. 1 and 3

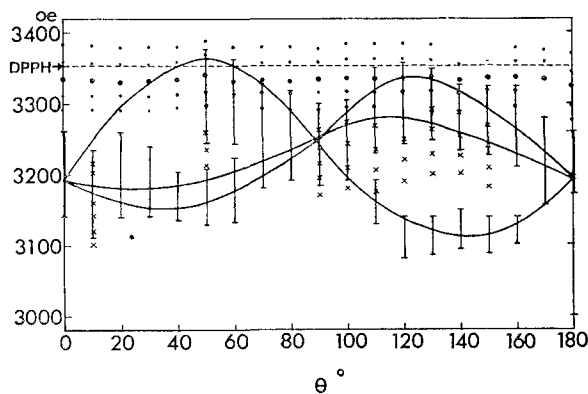


Fig. 3. Angular variation of electron paramagnetic resonance spectra of γ -ray irradiated $\text{CdCl}_2:\text{Ag}$. Measurement is made at liquid air temperature. Static magnetic field is rotated in the plane $\phi=72^\circ$. Solid dots denote positions of sharp isotropic lines (Ag-B lines), large dots are positions of central peaks, cross points denote positions of resolved hyperfine lines of $\text{Ag}^{++}\text{-Cl}^-$, solid curves are calculated positions for Ag-A bands, vertical lines show positions of broad band due to Ag^{++} , and their lengths show peak-to-peak widths of broad bands.

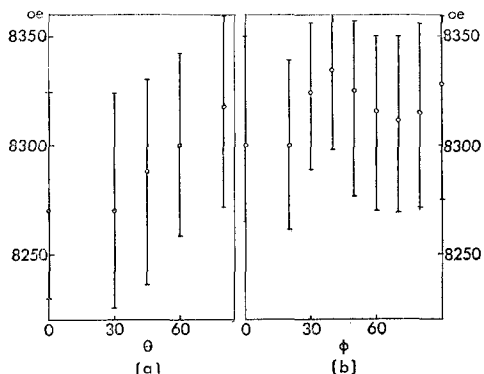


Fig. 4. Angular variation of electron paramagnetic resonance spectra of γ -ray irradiated $\text{CdCl}_2:\text{Ag}$ (-100°C). K-band microwave is used.

(a) Static magnetic field is rotated in a plane containing crystal c -axis. θ denotes angles between static magnetic field and c -axis.

(b) Static magnetic field is rotated in the plane perpendicular to crystal c -axis. ϕ denotes direction of static magnetic field measured from an arbitrary direction.

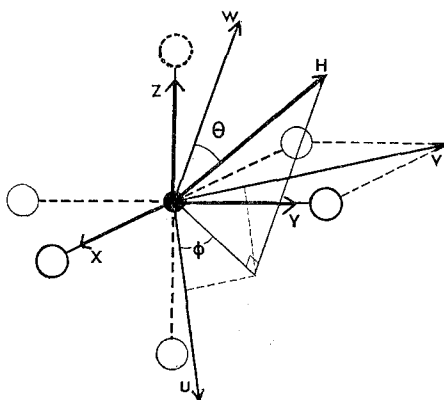


Fig. 5. Octahedral environment of substitutional Ag^{++} ion. Solid large circles show Cl^- ions, dotted line circle shows Cl^- ion vacancy and black circle shows Ag^{++} ion. u , v and w system is rotated from x , y and z system with a Euler angle $\alpha=45^\circ$, $\beta=\cos^{-1}(1/\sqrt{3})$ and $\gamma=0$, w -axis is parallel to crystal c -axis. \mathbf{H} shows a direction of static magnetic field (θ , ϕ).

are the above described patterns. Three solid curves in Fig. 3 show the positions of such patterns calculated with the use of Eq. (2) described below. The agreement of the observed pattern positions with the calculated ones is good.

The resolved lines on the broad band are hyperfine structure of silver and chlorine, we shall return to this point later.

It is convenient to choose new coordinate system u , v and w , whose w -axis is parallel to crystal c -axis. Euler angles of the transformation from x , y and z system to u , v and w system are $\alpha=45^\circ$, $\beta=\cos^{-1}(1/\sqrt{3})$ and $\gamma=0$. Then, spin Hamiltonian describing the position of a pattern corresponding to the tetragonal deformation of z direction is as following in the u , v and w system:

$$H = \beta [g_{uu} S_u H_u + g_{vv} S_v H_v + g_{ww} S_w H_w + g_{uw} (S_u H_w + S_w H_u)]. \quad (1)$$

Anisotropy of g value is described as :

$$g = \{ (g_{uu} \sin \theta \cdot \cos \phi + g_{uv} \cos \theta)^2 + g_{vv}^2 \sin^2 \theta \cdot \sin^2 \phi + (g_{vw} \cos \theta + g_{uw} \sin \theta \cdot \cos \phi)^2 \}^{1/2}, \quad (2)$$

where θ is angle between w-axis and the static magnetic field, ϕ denotes angle between u-axis and the projection of static magnetic field on u-v plane. Values of g tensors which satisfy the observed spectra are as followings :

$$\begin{aligned} g_{ww}^2 + g_{uv}^2 &= 4.4184, \\ g_{uu}^2 + g_{vw}^2 &= 4.2929, \\ g_{vv}^2 &= 4.2860, \\ g_{vw}(g_{vw} + g_{uu}) &= 0.3459. \end{aligned} \quad (3)$$

As nuclear spin of silver is $I=1/2$ (Ag¹⁰⁷, 51%; Ag¹⁰⁹, 49%), every pattern might have two h. f. s. and totally six h. f. s. lines might be observed but in fact patterns remained unresolved in much cases and only within the range of $\theta=100^\circ \sim 150^\circ$ one of the three patterns was resolved into about five lines with the intervals of about 30 gauss. Such hyperfine lines may be due to equal interactions of an unpaired electron spin with the nuclear spin of a silver ($I=1/2$) and that of a chlorine ($I=3/2$). According to this model the predicted line intensity ratio is 1:2:2:2:1 and this agrees with the observed intensity ratio of resolved five lines in the spectra.

Above described phenomena suggest that an unpaired electron of Ag⁺⁺ interacts only with one Cl⁻ nuclear spin of octahedral environment and the opposite side of Ag⁺⁺ ion to the interacting Cl⁻ ion is vacant. After all, a Cl⁻ ion vacancy associates with Ag⁺⁺ ion and this deforms octahedral environment tetragonally. Spin Hamiltonian including this hyperfine interaction is given as :

$$H = g\beta\mathbf{H} S_z' + [I_z'^{Cl} \{ (A_o^{Cl} + 2A_D^{Cl})^2 \cos^2 \theta + (A_o^{Cl} - A_D^{Cl})^2 \sin^2 \theta \}^{1/2} + I_z'^{Ag} + \{ (A_o^{Ag} + 2A_D^{Ag})^2 \cos^2 \theta + (A_o^{Ag} - A_D^{Ag})^2 \sin^2 \theta \}^{1/2}] S_z', \quad (4)$$

where S_z' , $I_z'^{Cl}$ and $I_z'^{Ag}$ are electron spin quantum number, nuclear spin quantum number of Cl and Ag with respect to the quantization axis, respectively; A_o^{Ag} , A_o^{Cl} : contact hyperfine constants of Ag and Cl; A_D^{Ag} , A_D^{Cl} : dipole hyperfine constants of Ag and Cl. Values of hyperfine constants are as followings : $\frac{|A_o^{Cl}|}{g\beta} \sim \frac{|A_o^{Ag}|}{g\beta} \sim 30$ gauss and A_D are not evident.

(B) **Ag-B lines.** They consist of sharp five lines as shown in Figs. 1 and 2. Intensity ratio is about 1:5:10:5:1 and the value of g factor is 2.014. The distances between lines are equal and about 23 gauss independent of microwave frequency. Fig. 3 shows that they are isotropic. Intensity ratio of these lines to the Ag-A band are almost constant for various samples.

These lines may be due to the certain isotropic imperfection which captures an electron produced by γ -ray irradiation. As the isotropic imperfection, tetrahedrally aggregated four Ag⁺ ions or Cd⁺⁺ ions are most plausible. The former shows five hyperfine lines with the intensity ratio 1:4:6:4:1 and the latter shows nine lines with the intensity ratio 1:24:220:936:1720:936:220:24:1 as is shown in Fig. 9, in this case outer four lines are too small to be detected in comparison with the intensity of central line and five lines can be observed

II. 3. EPR Measurements of CdCl₂:Cu

A symmetric unresolved gaussian like pattern was observed at room temperature. Though the line shape was symmetric but a slight anisotropy appeared at the temperature of -100°C . In liquid air temperature, remarkable anisotropy appeared and at the certain values of θ resolved four hyperfine structure lines of cupric ion was observed as shown in Figs. 6 and 7.

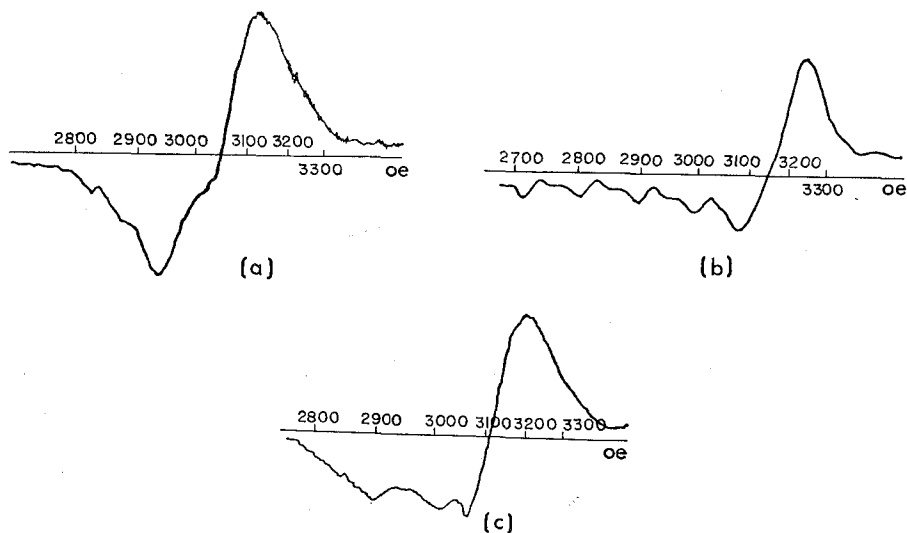


Fig. 6. Electron paramagnetic resonance spectra of γ -ray irradiated CdCl₂:Cu. Measurement is made at liquid air temperature and x-band microwave is used. Direction of static magnetic field is (a) parallel to *c*-axis, (b) $\theta=40^{\circ}$, $\phi=0^{\circ}$ (c) $\theta=140^{\circ}$, $\phi=0^{\circ}$.

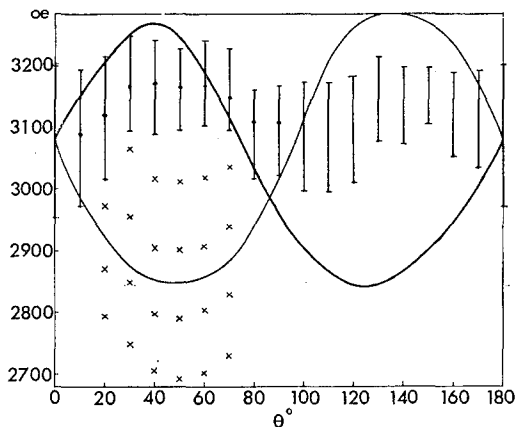


Fig. 7. Angular variation of electron paramagnetic resonance spectra of γ -ray irradiated CdCl₂:Cu. Measurement is made with x-band microwave at liquid air temperature. Static magnetic field is rotated in the plane $\phi=0^{\circ}$. Cross points denote positions of resolved hyperfine lines of cupric ion in the substitutional sites. Vertical lines show positions of unresolved broad band due to cupric ions, and their lengths show peak-to-peak widths of broad band. Solid curves show calculated positions for substitutional cupric ions, and thick curve means overlapping of two bands.

Explanation of the observed spectra can be done in the same way as in the case of Ag-A band except the hyperfine structure. Though in the case of Ag-A band the hyperfine interaction of a Ag⁺⁺ and one Cl⁻ ion is observed, only four hyperfine structure lines of cupric ion itself are observed in this case.

Anisotropic behaviour of spectra in Fig. 7 can be explained with the Eq. (1) using the following values of g tensors :

$$\begin{aligned} g_{ww}^2 + g_{uw}^2 &= 4.783, \\ g_{uu}^2 + g_{uw}^2 &= 4.987, \\ g_{vv} &= 2.362, \\ g_{uv}(g_{vw} + g_{wu}) &= 0.759. \end{aligned} \quad (5)$$

Solid curves in Fig. 7 were calculated from Eq. (1) with the values of (5). Hyperfine constant $\frac{|A|}{g\beta}$ was obtained to be about 110 gauss.

III. DISCUSSION

III. 1. Ag-A Band

In general, Zeeman term of spin Hamiltonian for a tetragonal environment (tetragonal axis is parallel to z-axis) and an axial field parallel to its (111) direction is given as follows :

$$\begin{aligned} H_{zeeman} = \beta [&g_{zz}H_z S_z + g_{xx}(H_x S_x + H_y S_y) \\ &+ g_{xz}(H_x S_z + H_z S_x + H_y S_z + H_z S_y) + g_{xy}(H_x S_y + H_y S_x)]. \end{aligned} \quad (6)$$

Eq. (1) and Eq. (2) can be obtained by transforming Eq. (6) into the u, v and w system. If the tetragonal deformation is parallel to x-axis or y-axis, Zeeman term can be obtained by rotating the angle ϕ by 120° or 240° for respective case.

In the case of Ag-A band, Zeeman term for three tetragonal axes (x, y and z directions) can be calculated with the use of Eq. (2) and the values of (3) and obtained a good agreement with the observed spectra as shown in Fig. 3. According to this fact, it is easy to recognize that Ag⁺⁺ ions occupy substitutional metallic sites in crystal.

It may be supposed that resolved lines are due to the hyperfine interaction of unpaired electron spin and nuclear spin of Ag⁺⁺ ($I=1/2$, Ag¹⁰⁷, Ag¹⁰⁹) and that of Cl⁻ (Cl³⁵, Cl³⁷, $I=3/2$). As the result of tetragonal deformation, certain special Cl⁻ ions may come to nearer sites to Ag⁺⁺ ion than other Cl⁻ environment ions, then nuclear spins of such nearer Cl⁻ ions may interact with an unpaired electron of Ag⁺⁺ ion. In such a case where two Cl⁻ ions in the opposite sites with respect to Ag⁺⁺ ion are nearer to the Ag⁺⁺ ion than other four Cl⁻ ions, hyperfine structure lines are eight with the intensity ratio of 1:3:5:7:7:5:3:1 providing that the hyperfine interaction constants of silver and chlorine are equal. But, if one of the Cl⁻ ions in the octahedral environment is vacant and only one Cl⁻ ion opposite to the vacancy with respect to Ag⁺⁺ ion can interact with an unpaired electron of Ag⁺⁺, hyperfine lines are five and their intensity ratio is 1:2:2:2:1. Observed resolved lines may agree with the latter case. That is, we can conclude that a Cl⁻ ion vacancy still associates with substitutional silver ion after the Ag⁺ has been converted to Ag⁺⁺ with γ -ray irradiation.

The existence of a coupling between Ag^{++} ion and one Cl^- ion which is placed at the opposite side of Cl^- ion vacancy suggests that the tetragonal deformation is compressed one and ground state of Ag^{++} ion is orbital singlet $E\theta$ (symmetry d_{z^2}) instead of $E\epsilon$.⁵⁾ This is consistent with the fact that the value of g_{ww} is larger than that of g_{uu} in the case of the ground state $E\theta$. The values of g tensor show considerable agreements with that of Ag^{++} in KCl .⁶⁾

III. 2. Ag-B Lines

Two possible models are considered.

[1] Electron trapped in the tetrahedral aggregate of Ag^{++} ions. AgCl crystal has *f.c.c.* lattice and layers of Ag^+ ions and Cl^- ions are parallel to $[111]$ plane and piled alternately. CdCl_2 crystal has layers of Cl^- parallel to $[111]$ plane and layers of Cd^{++} are inserted between them, but vacant layers are remained alternately. Due to the similarity of both crystal structures, $\text{CdCl}_2:\text{Ag}$ crystal might reserve AgCl structure locally in it, then the tetrahedral aggregate of Ag^+ ions can exist in CdCl_2 as shown in Fig. 8. If an electron produced by γ -ray irradiation may be trapped in this aggregate, it travels through $5s$ orbitals of four Ag^+ ions and interacts with nuclear spins of Ag^+ ions showing five lines with a intensity ratio of 1:4:6:4:1.

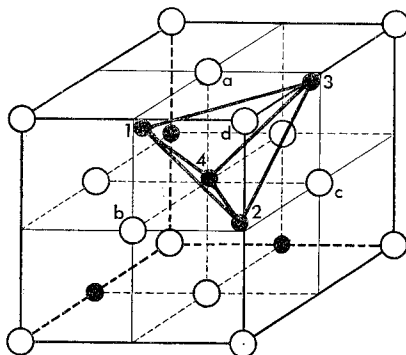


Fig. 8. The proposed model for Ag-B center. White circles are Cl^- ions and dark circles positive ions. Four positive ions 1, 2, 3 and 4 compose a tetrahedron. If an electron is trapped in this aggregate, it travels through these four metal ions and interacts with their nuclear spins. If positive ions are Ag^+ , positive ions 1, 2, 3, 4, negative chlorine ions a, b, c and d reserve the AgCl structure in CdCl_2 crystal. If positive ions are Cd^{++} , positive ions 1, 2 and 3 are in the regular sites and the 4 is in the interstitial site of CdCl_2 structure.

[2] Electron trapped in the tetrahedral aggregate of Cd^{++} ions.

When Cd^{++} ion in lattice site captures an electron produced by γ -ray irradiation and becomes Cd^+ ($4d$)¹⁰ ($5s$)¹, it may become unstable in lattice site, if this Cd^+ ion is released from lattice site and placed at interstitial site, it may construct a tetrahedral aggregate of Cd^{++} ions with three other Cd^{++} ions in the regular sites. Electron captured in Cd ion may migrate around four $5s$ orbitals of Cd^{++} ions. In this case, as the odd isotopes of cadmium are Cd^{111} ($I=1/2$, 12.75%) and Cd^{113} ($I=1/2$, 12.26%), hyperfine structure may be observed as the superposition

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of five patterns as shown in Fig. 9, and nine lines are expected. If we consider that only five intense lines of central part among those nine lines are detectable, this model does not contradict with observed spectra.

Further investigations are necessary to determine the model of Ag-B center. It is also future problem whether these lines have some relations with a strong absorption of light at near 5000 Å or not.

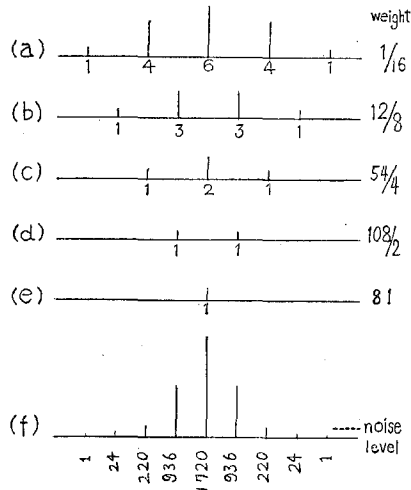


Fig. 9. Predicted spectra for a trapped electron at the tetrahedral aggregate of Cd⁺⁺ ions.

- (a) Spectrum for the case where all Cd⁺⁺ ions in the tetrahedral aggregate are odd isotopes.
- (b) Three Cd⁺⁺ ions in the tetrahedral aggregate are odd isotopes.
- (c) Two Cd⁺⁺ ions in the tetrahedral aggregate are odd isotopes.
- (d) One Cd⁺⁺ ion in the tetrahedral aggregate is odd isotope.
- (e) All Cd⁺⁺ ions of the tetrahedral aggregate are even isotopes.
- (f) Superposition of spectra (a) (b) (c) (d) and (e). Intensity ratio is given under the lines.

III. 3. CdCl₂:Cu

Since g_{uu} exceeds g_{ww} , $E\epsilon$ may be ground state and octahedral environment may suffer an elongated deformation. Whether the Cl⁻ vacancy is associated to Cu⁺⁺ ion is not evident.

IV. CONCLUSION

In CdCl₂:Ag irradiated with γ rays at room temperature, two kinds of paramagnetic centers are found. One of them is γ -ray induced Ag⁺⁺ which is substituted for metallic site in crystal. Further, it is found that a Cl⁻ ion vacancy is associated with the Ag⁺⁺ ion and the environment of Ag⁺⁺ is compressed tetragonally. And it can be concluded that the ground state of this Ag⁺⁺ ion is $E\theta$.

For the other paramagnetic center, it can be assumed that the center is composed of an electron and the tetrahedral aggregate of metal ions, but it is future problem to determine whether the metal ion is Ag⁺ or Cd⁺⁺.

In γ -ray irradiated $\text{CdCl}_2 : \text{Cu}$, substitutional Cu^{++} center is found. Environment of Cu^{++} is considered to be elongated tetragonal and its ground state may be $E\epsilon$.

V. ACKNOWLEDGEMENT

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