ESR of Hot Ions: Zn(I), Cd(I), and Hg(I) in γ-Irradiated Potassium Tetracyano Zincate(II), Cadmate(II), and Mercurate(II)

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It is known that X-ray or γ-ray irradiation of inorganic complexes produces hot ions which have lower valence states than the original ones and yet are sited in the regular crystalline array of the undamaged mother complexes. ESR study reveals that the hot ions of paramagnetic Zn(I), Cd(I), and Hg(I) complexes are formed by γ-irradiation of $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$, respectively. Hyperfine structures of the ESR signals shows that the Zn(I) and Cd(I) complexes have C_{3v} symmetry instead of T_d symmetry of the original complex, and Hg(I) complex has a slightly distorted C_{3v} symmetry. In Zn(I) complex, one of the four symmetry axes along Zn(II)–CN bondings is stretched. This occurs evenly with respect to each axis, resulting in the formation of four sites of the electron spins. For Cd(I) complexes, four species are produced as an irradiation product, where each species has four sites which are axially symmetric with respect to any one of the four Cd(II)–CN bondings. In Hg(I) complex, there exist twenty-four sites and the symmetry axis of each site lies along a direction slightly deviated from the original Hg(II)–CN bonding. From the behavior of the decay of ESR signal intensity at liquid nitrogen temperature, it is concluded that the stability is in the order Hg(I)>Cd(I)>Zn(I).

X-ray or γ-ray irradiation of diamagnetic substances results in the production of ESR active paramagnetic centers. It has been found that the central metal ions are reduced to the lower valence state in the case of X-ray or γ-ray irradiated Co(III) or Pd(II) complexes.[1–5] These metastable paramagnetic centers have been referred to as hot ions[5] because they are hot (unstable) in the sense that the valence state differs from that of the original complex and yet they are sited in the host lattices of the original complex.

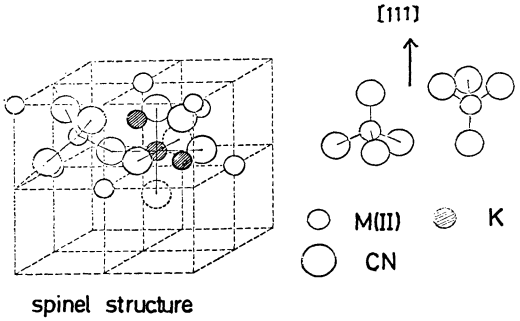

Fig. 1. Crystal structure of $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$.
$M(II)(CN)_4$ forms a regular tetrahedron with four M(II)-CN bondings aong [111], [1$\bar{1}\bar{1}$], [$\bar{1}$1$\bar{1}$], and [$\bar{1}\bar{1}$1].
The figure of spinel structure is quoted from E.W. Gorter *Philips Res. Repts.* **9**, 295, (1954).

Since Zn(II), Cd(II), and Hg(II) ions are formed of closed *d*-shell, the reduced ions Zn(I), Cd(I), and Hg(I) are expected to have an unpaired electron of large *s*-character. No report has so far been found with regard to the presence of stable complex of Zn(I). The only example reported is of $Cd_2[AlCl_4]_2$. However, as it is a diamagnetic diatomic ion,[6] no ESR signal is expected. The situation is the same with all stable Hg(I) salts such as Hg_2Cl_2. The existence of paramagnetic Zn(I) and Cd(I) ions was evidenced in the γ-ray irradiated frozen solutions of Zn(II) or Cd(II) salts.[7,8] ESR was observed with Cd(I) ion which was isolated in the matrix of rare gas.[9] All the systems referred to in literature are amorphous with respect to the host lattices, and not crystalline. We carried out ESR investigation with single crystals of Zn(II), Cd(II), and Hg(II) complexes. Formation of hot ions of paramagnetic Zn(I), Cd(I), and Hg(I) by γ-ray irradiation was evidenced. The total dose of γ-rays was made to not exceed the magnitude with which the host lattices are destroyed. It is expected that the metastable M(I) complexes are formed in the mother compounds, where M(I) refers to either one of Zn(I), Cd(I), or Hg(I). It will be shown that the crystal fields of the M(I) ions still keep the symmetry properties of the mother compounds fairly well. The location of the electron spins and the bonding nature of Zn(I), Cd(I), and Hg(I) ions are elucidated. It should be noted that the hot ions can be used for making possible ESR investigation of diamagnetic inorganic complexes which are normally ESR insensitive.

Experimental

Compounds investigated were potassium tetracyanozincate(II) $K_2[Zn(CN)_4]$, potassium tetracyanocadmate(II) $K_2[Cd(CN)_4]$, and potassium tetracyanomercurate(II) $K_2[Hg(CN)_4]$. Single crystals of $5\times10\times10$ mm^3 are easily obtained by slow evaporation of aqueous solution. They exihibit the faces of the octahedron (111), generally tabular in habit. Dickinson[10] confirmed that $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$ have a spinel structure with the tetrahedral

1) W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **49**, 2883 (1968).
2) J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Structure*, **1**, 127 (1968).
3) S. Fujiwara and M. Nakamura, *J. Chem. Phys.*, **52**, 6299 (1970).
4) S. Fujiwara and M. Nakamura, *J. Coord. Chem.*, in press.
5) S. Fujiwara, T. Watanabe, and H. Tadano, *ibid.*, in press.
6) J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).
7) P. N. Moorthy and J. J. Weiss, *Nature*, **201**, 1318 (1964).
8) R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. A*, **1970**, 3080.
9) P. H. Kasai, *Phys. Rev. Lett.*, **21**, 67 (1968).
10) R. G. Dickinson, *J. Amer. Chem. Soc.*, **44**, 774 (1922).

complex ion $[M(II)(CN)_4]^{2-}$. The direction of the four M(II)–CN bondings in the tetrahedral complex ion are parallel to the crystallographic axes [111], [1$\bar{1}\bar{1}$], [$\bar{1}$1$\bar{1}$], and [$\bar{1}\bar{1}$1]. The neutron diffraction study by Sequeira and Chidambaram[11] confirmed that $[Zn(CN)_4]^{2-}$ forms a regular tetrahedron.

The crystals and powder samples were exposed to γ-rays from a ^{60}Co source in a vacuum ($\sim$1 mmHg) or nitrogen atmosphere with a dose rate of 5×10^4 R/hr for 20 hr at 77°K. After irradiation, ESR spectra were recorded at 77°K by a JEOL 3BS X-band spectrometer and a JEOL SK-1 K-band spectrometer using 100 kHz field modulation. On irradiation, the color of the crystals turned reddish orange (Zn), yellow (Cd), and orange (Hg). When the crystals were taken out of the liquid nitrogen Dewar vessel into the air, the color diminished rapidly and the ESR signals of M(I) complexes disappeared. Single crystals were attached to a glass or Teflon rod, and irradiated by γ-rays in a liquid nitrogen Dewar vessel. After irradiation they were transferred immediately to another Dewar vessel for ESR measurements. Powders were sealed in one end of a quartz tube and subjected to irradiation. After irradiation, the tube was quickly turned upside down, the sample being transferred to the other end which had been protected from irradiation. ESR measurements were performed twice, first with the sample in the γ-ray irradiated end and then in the other non-irradiated end. In the first measurement, the doublet signal of H atom observed beside the signal of hot ions was used as the reference for the field sweep caliblation. The H atom is assumed to have been produced by irradiation in the quartz tube. Inversion of the sample tube was carried out as quickly as possible to make the decrease of the signal intensity negligible.

Results and Discussion

The spectra of γ-irradiated powder $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$ are shown in Figs. 2—5, where signals of radicals (central sharp line) and metal complexes can be seen. The latter was mainly examined. All the spectra show hyperfine structures of fairly large splitting constants, g value of about 2 and isotropic and small linewidth. The results can be interpreted in terms of the electronic configuration of $nd^{10}(n+1)s^1$ (n=3, 4, and 5 for Zn, Cd, and Hg, respectively). Thus the products of γ-irradiation are the cyano complex of Zn(I), Cd(I), and Hg(I). The location of the electron spin in the outer shell was investigated. Two locations are possible, spherical isotropic distribution in the outermost s shell and that confined in any one of the four metal-cyano bondings. The crystal structure of the mother compounds is of the spinel type. If the structure of tetrahedron symmetry of the mother compound is maintained and the electronic distribution is completely spherical in $[M(I)(CN)_4]^{3-}$, a simple spectrum of a single line or of hyperfine structure is expected. No angular de-

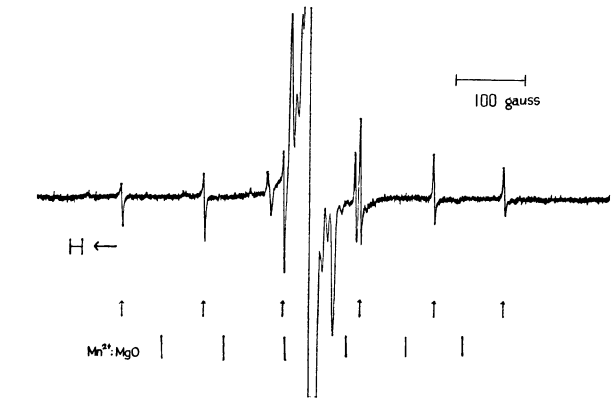

Fig. 2. The powder spectrum of γ-irradiated $K_2[Zn(CN)_4]$ (X-band, 100 kHz modulation, at 77°K)
The strong absorption in the center is the signal of Zn(I) with no nuclear spin. Six arrows indicate ^{67}Zn(I) hyperfine structure. Other signals near the center are those of radicals.

11) A. Sequeira and R. Chidambaram, *Acta Crystallogr.*, **20**, 910 (1966).

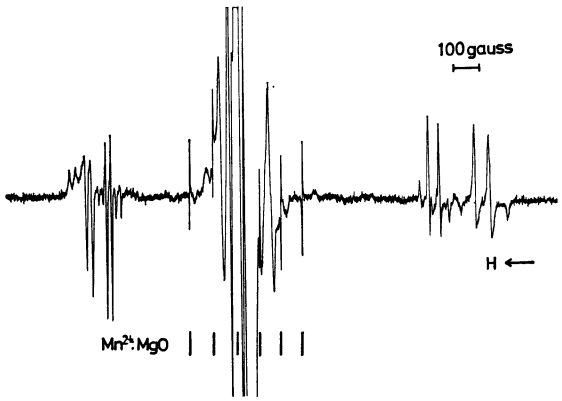

Fig. 3(a). The powder spectrum of γ-irradiated $K_2[Cd(CN)_4]$. (X-band, 100 kHz field modulation, at 77°K)
The spectrum indicates that four species are produced.

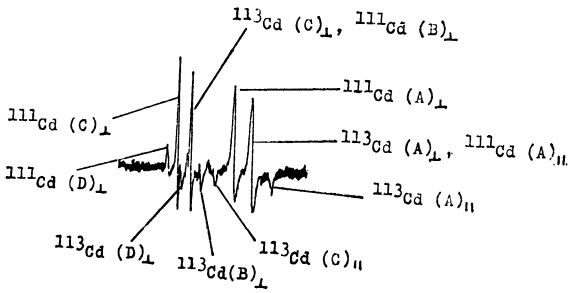

Fig. 3(b). Assignment of Cd(I) species in the low field.

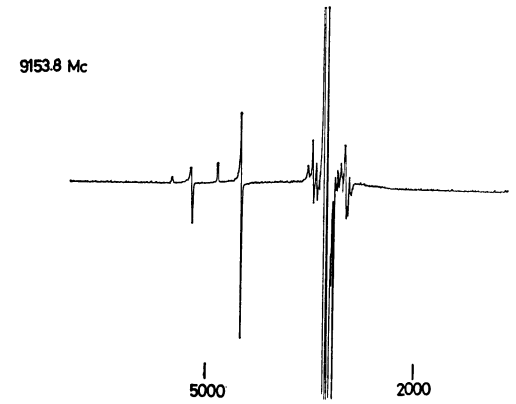

Fig. 4. The powder spectrum of γ-irradiated $K_2[Hg(CN)_4]$. (X-band, 100 kHz modulation, at 77°K)
The signal in 5400 gauss is the fourth line of ^{201}Hg hyperfine structure. The signal in 4600 gauss is the second line of ^{199}Hg hyperfine structure.

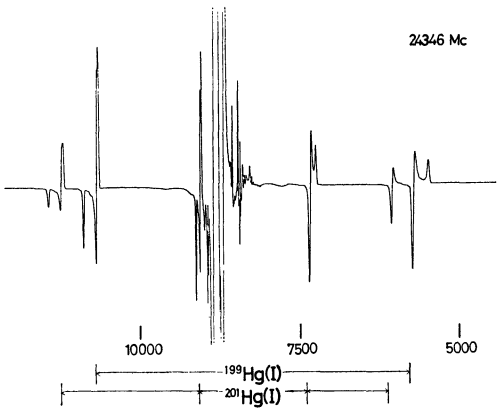

Fig. 5. The powder spectrum of γ-irradiated $K_2[Hg(CN)_4]$. (K-band, 100 kHz field modulation, at 77°K)
Full hyperfine structure can be observed at this frequency. The large hyperfine structure constants shift the apparent g-value far away from the position of $g=2$. The shoulder in the perpendicular line in the high field shows a slight deviation from axial symmetry.

pendence is expected with respect to the spectrum of single crystal samples. The results show angular dependence eliminating the spherical distribution of spins, and suggest that M(I) ions are in C_{3v} field. Namely, the electron spins in $[M(I)(CN)_4]^{3-}$ occupy the outermost s orbital but are confined in one of the four bondings. Detailed results will be given in the following.

(1) γ-Irradiated $K_2[Zn(CN)_4]$. The spectrum consists of a single strong line ($g=2$) and six satellite lines (the spectrum of this structure will be referred to as a set). The satellites are attributed to the isotope of ^{67}Zn ($I=5/2$) with a natural abundance of 4.11%. The intensity ratio of satellites to the central signal agrees with the abundance ratio of isotopes.

The single crystal shows a spectrum of four sets which suggests the coexistence of four sites for the distribution of electron spin. Angular variation cannot be seen distinctly with respect to the g value, but clearly with A values. Hence, the symmetry of Zn(I) complexes is fairly accurately determined by an examination of the angular dependence of hyperfine structure. An example of a γ-irradiated single crystal of $K_2[Zn(CN)_4]$ being rotated around [111] axis which is perpendicular to the static magnetic field is shown in Fig. 6. During the rotation, the crystallographic face [111] preserved the direction parallel to the magnetic field, in which one site is invariant and the relation of the remaining three sites displays threefold rotational

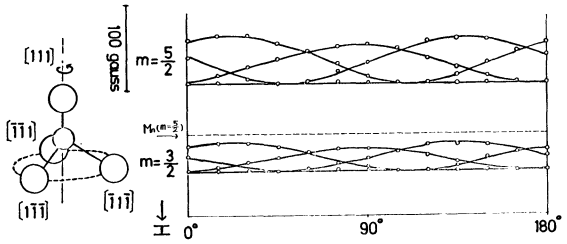

Fig. 6. Anglular dependence of the hyperfine structure lines of γ-irradiated single crystal of $K_2[Zn(CN)_4]$ with respect to the rotation of the crystal around $[111]\perp H$.
(X-band, 100 kHz field modulation, at 77°K)

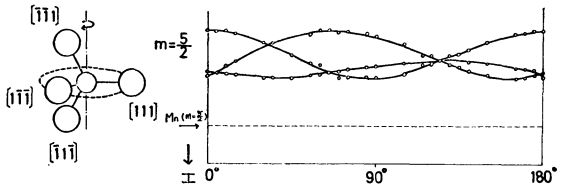

Fig. 7. Anglar dependence of hyperfine structure lines of γ-irradiated single crystal of $K_2[Zn(CN)_4]$ with $[0\bar{1}1]\perp H$. In this rotation, [111] and $[1\bar{1}\bar{1}]$ varies from 0° to 90° against H. The largest splitting occurs where one of these two axis is parallel to H. The samllest splitting occurs where H becomes perpendicular to Zn(II)-CN direction.

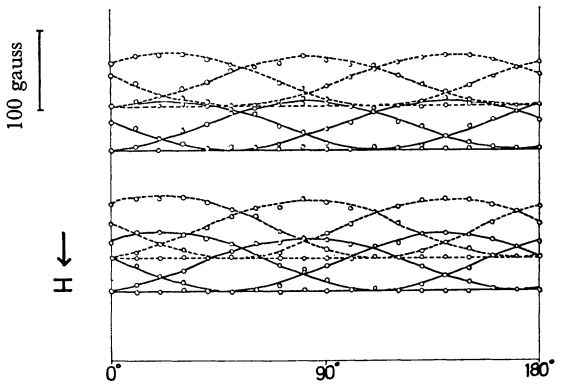

Fig. 8(a). Angluar dependence of hyperfine structure lines of γ-irradiated single crystal of $K_2[Cd(CN)_4]$ with the rotation with $[111]\perp H$ (the lines in the low field).
——^{113}Cd, ------^{111}Cd
The sets of lines appearing on the outer side are of species A and those on in the inside species C.

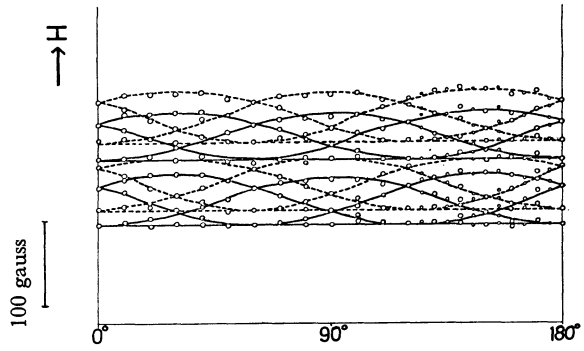

Fig. 8(b). Angular dependence of hyperfine structure lines of γ-irradiated single crystal of $K_2[Cd(CN)_4]$ with rotation with $[111]\perp H$ (the lines in the higher field).

symmetry with respect to the [111] axis. The results of the rotation $[0\bar{1}1]$ axis perpendicular to the static field are given in Fig. 7. The crystal rotates with the [111] face parallel to the rotational axis. Two sites show the same variation with an interval of the tetrahedral angle and the other two are found to be equivalent. At the positions of the crystal where the static field bisects the tetrahedral angles, four sites of lines collapse into one.

It is to be noted that if g-tensor and A-tensor of Zn(I) are (within experimental error) axially symmetric along the Zn–CN bond of the original complex ion $[Zn(CN)_4]^{2-}$, the angular dependence of its ESR spectrum can be readily inferred. When one of the four Zn(II)–CN directions in the host crystal, [111], $[1\bar{1}\bar{1}]$,

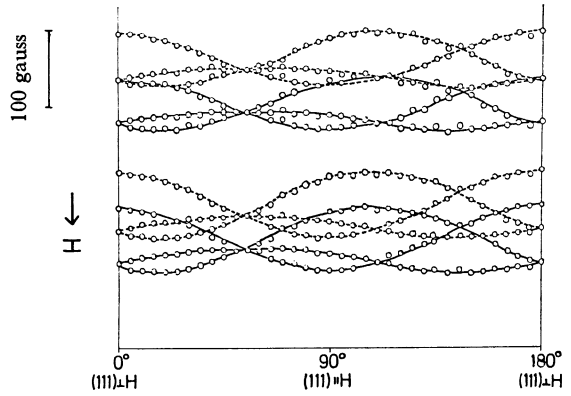

Fig. 9(a). Angluar dependence of hyperfine structure lines of γ-irradiated single crystal of $K_2[Cd(CN)_4]$ with rotation with $[0\bar{1}1]\perp H$ (the lines in the low field).

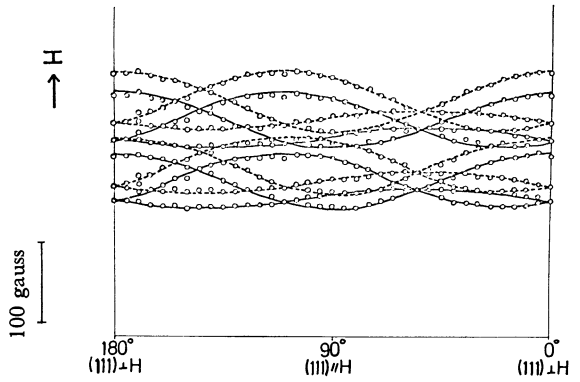

Fig. 9(b). Angular dependence of hyperfine structure lines of γ-irradiated single crystal of $K_2[Cd(CN)_4]$ with rotation with $[0\bar{1}1]\perp H$ (the lines in the higher field).

$[\bar{1}\bar{1}1]$, and $[\bar{1}1\bar{1}]$, is parallel to the static field, the corresponding site shows the largest splitting. The smallest splitting occurs when one of the axes is perpendicular to the static field. It is thus concluded that the paramagnetic Zn(I) complex is axially symmetric with respect to the symmetry axis along Zn(II)–CN bonding of the host lattice. Since each Zn(II)–CN bonding coincides with the threefold symmetry axis in the original complex $[Zn(CN)_4]^{2-}$, it is probable that the Zn(I) complex has C_{3v} symmetry instead of T_d symmetry. As the four Zn(II)–CN bondings are equivalent in the original complex $[Zn(CN)_4]^{2-}$, the location of the spin is assumed to be of equal probability with respect to all four bondings. Hence, in the Zn(I) complex produced by γ-ray irradiation, one of the Zn(II)–CN directions becomes the unique axis, and such a distortion is assumed to occur evenly with respect to the four bondings. Thus the symmetry is lowered from T_d to C_{3v}. The signal intensities indicate that four sites are produced in an equal quantity.

ESR parameters are calculated by the following spin Hamiltonian:

$$\mathcal{H}=\beta\mathbf{S}\cdot\mathbf{G}\cdot\mathbf{H}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} \quad (1)$$

In the case of $[Zn(I)(CN)_4]^{3-}$, the high field approximation is adopted satisfactorily. Under conditions where the g-tensor and A-tensor are axially symmetric about the same axis, the solution of the spin Hamiltonian has been given by Abragam and Bleany.[12]

$$h\nu=g\beta H+Km+\frac{B^2}{4g\beta H}\left(\frac{A^2+B^2}{K^2}\right)\{I(I+1)-m^2\}+\frac{1}{2g\beta H}\left(\frac{A^2-B^2}{K}\right)\left(\frac{g_{//}-g_{\perp}}{g^2}\right)\sin^2\theta\cos^2\theta m^2 \quad (2)$$

$$K^2g^2=A^2g_{//}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta \quad (3)$$

($S=1/2$, $I=5/2$, quadrupole term is not taken into account.)

Using Eq. (2), we obtain for $[^{67}Zn(I)(CN)_4]^{3-}$:

$g_{//}=2.000\pm0.005$ $\quad g_{\perp}=1.999\pm0.005$
$A=131\pm1$ gauss $\quad B=110\pm1$ gauss

For $[Zn(I)(CN)_4]^{3-}$ of zinc isotopes with no nuclear spin we get:

$g_{//}=2.001\pm0.005$ $\quad g_{\perp}=1.999\pm0.005$

(2) γ-Irradiated $K_2[Cd(CN)_4]$. Of the stable isotopes of cadmium, two isotopes, ^{111}Cd ($I=1/2$, natural abundance 12.86%) and ^{113}Cd ($I=1/2$ natural abundance 12.34%), possess nuclear spins. In accordance with the constitution of isotopes, the ESR spectrum of the irradiated compound shows two sets of hyperfine lines. One set with larger splitting refers to that of ^{113}Cd which has a larger absolute value of magnetic moment. The signals of the isotopes of zero nuclear spin cannot clearly be distinguished from those of radicals.

We see from the spectrum of powdered sample (Fig. 3) that four different species of the Cd(I) complexes are produced for each isotope. These species are denoted by A, B, C, and D in decreasing order of magnitude of hyperfine splitting. Each species differs with regard to the value of hyperfine splitting, signal intensity, behavior of the decay at 77°K and linewidth.

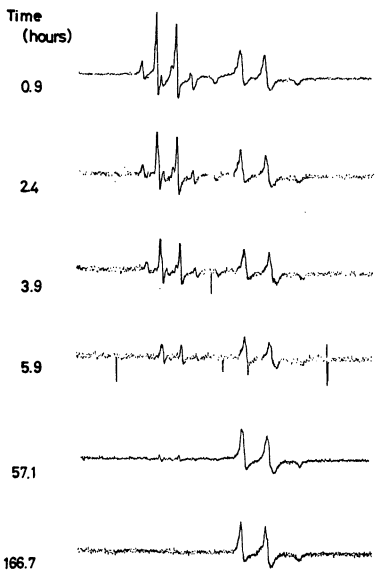

Fig. 10. Decay behaviour of Cd(I) complex (powder, non-degassed, at 77°K)
Intensities are almost normalized by Mn^{2+} signal present in the sample. Species A is sable at this temperature. Other species decay into nothing.

12) A. Abragam and B. Bleany, "Electron Paramagnetic Resonance of Transition Ions.," Clarendon Press, Oxford (1970), p. 173.

Immediately after irradiation, the signal intensity of each species is in the order C>A≫B~D. The intensity of B and D is very small. At 77°K, B, C, and D decay with the half-life of about 1/2 day. A which shows the largest hyperfine splitting is stable at this temperature in non-degassed sample. The decay behavior is shown in Fig. 10.

The number of sites and the symmetry of the Cd(I) complexes were determined by single crystal spectra. The results of experiments where γ-irradiated single crystal of $K_2[Cd(CN)_4]$ was rotated around the [111] axis and the [0$\bar{1}$1] axis perpendicular to the static magnetic field are given in Figs. 8 and 9, respectively. Measurements of the ESR spectra of B and D could not be carried out owing to the weakness of intensity. The angular dependence of these species is assumed to be similar to that of A and C in the whole range of rotation. This is confirmed by the fact that at the direction where the four sites of A and C merge in one, four sites of B and D also collapse in one. We thus assume that the number of sites and the angular variation of each species are the same except for the magnitude of the splitting. The same is assumed to hold for Zn(I) complex. Thus the hyperfine spectrum of Cd(I) consists of 2 (isotopes) $\times$ 4 (species) $\times$ 4 (sites). Each species has four sites axially symmetric with respect to the Cd(II)–CN direction in the host lattice, [111], [1$\bar{1}\bar{1}$], [$\bar{1}$1$\bar{1}$], and [$\bar{1}\bar{1}$1]. The paramagnetic Cd(I) complex is stretched along the symmetry axis (z-axis) which is parallel to any one of the four Cd(II)–CN directions in the host lattice. It was thought that the reduction of Cd(II) to Cd(I) might accompany the distortion of the mother complex, particularly that along the Cd(II)–CN bonding. As in the case of $K_2[Zn(CN)_4]$, γ-irradiation produced Zn(I) ion with C_{3v} symmetry. We assume that this holds with Cd(I), but in this case four species are produced. We take it for granted that the distortion occurs along Cd(II)–CN bonding with four different magnitudes in each Cd(II)–CN direction, resulting in the formation of the four species.

The parameters of ESR hyperfine spectrum are calculated for A and C by Eq. (1). For both isotopes ^{111}Cd(I) and ^{113}Cd(I), $S=1/2$ and $I=1/2$. In this case, the hyperfine splitting is too large for application of high field approximation. If the principal axes of the g- and A-tensors are taken to be parallel and the static magnetic field parallel to one of the principal axes, Eq. (1) can be exactly solved. With axial symmetry, the Hamiltonian becomes simpler. The method for $S=1/2$ and $I=1/2$ has been developed.[13]

The strongly allowed transitions under the experimental conditions are as follows. For the case of H parallel to the z-axis (symmetry axis), we have

$$h\nu=\frac{1}{2}g_{//}\beta H_1+\frac{1}{2}A+\frac{1}{2}[(g_{//}\beta H_1)^2+B^2]^{1/2}$$
$$h\nu=\frac{1}{2}g_{//}\beta H_2-\frac{1}{2}A+\frac{1}{2}[(g_{//}\beta H_2)^2+B^2]^{1/2} \quad (4)$$

For the case of H perpendicular to the z-axis, we have

$$h\nu=\frac{1}{2}\left[(g_\perp\beta H_1)^2+\left(\frac{A-B}{2}\right)^2\right]^{1/2}+\frac{1}{2}B+\frac{1}{2}\left[(g_\perp\beta H_1)^2+\left(\frac{A+B}{2}\right)^2\right]^{1/2}$$
$$h\nu=\frac{1}{2}\left[(g_\perp\beta H_2)^2+\left(\frac{A-B}{2}\right)^2\right]^{1/2}-\frac{1}{2}B+\frac{1}{2}\left[(g_\perp\beta H_2)^2+\left(\frac{A+B}{2}\right)^2\right]^{1/2} \quad (5)$$

Taking the difference in each two equations of Eqs. (4) and (5), the hyperfine splitting constants A and B are connected to the observed magnetic field values H_1 and H_2. The difference between the observed separation H_2-H_1 and the true hyperfine splitting constants A and B becomes smaller at higher microwave frequency. First, with the use of an approximate value of B for the observed separation in the K-band powder spectrum, Eq. (4) and the single crystal data with z-axis parallel to H give an approximate value of A. Due to the nearly isotropic nature of g-value, calculation is easy. With the use of the A value thus obtained and the observed value of the magnetic field for the single crystal spectrum with z-axis perpendicular to H as well as Eq. (5), a more appropriate value of B is obtained. This process is repeated until the values of A and B become consistent within experimental error. Next, $g_{//}$ and $g_\perp$ are calculated with the use of A and B thus obtained. The results are as follows.

Species A for ^{113}Cd (I)
$g_{//}=1.99\pm0.01$ $g_\perp=1.998\pm0.005$
$A=(1.58\pm0.01)\times10^3$ gauss
$B=(1.47\pm0.01)\times10^3$ gauss
for ^{111}Cd (I)
$g_{//}=1.99\pm0.01$ $g_\perp=1.998\pm0.005$
$A=(1.52\pm0.01)\times10^3$ gauss
$B=(1.40\pm0.01)\times10^3$ gauss
Species C for ^{113}Cd (I)
$g_{//}=2.00\pm0.01$ $g_\perp=1.986\pm0.005$
$A=(1.37\pm0.01)\times10^3$ gauss
$B=(1.23\pm0.02)\times10^3$ gauss
for ^{111}Cd (I)
$g_{//}=2.00\pm0.01$ $g_\perp=1.986\pm0.005$
$A=(1.31\pm0.01)\times10^3$ gauss
$B=(1.18\pm0.01)\times10^3$ gauss

(3) γ-Irradiated $K_2[Hg(CN)_4]$. The ESR spectrum of the γ-irradiated powder sample of $K_2[Hg(CN)_4]$ consists of the signals of the radicals and those of mercury isotopes of $I=0$, 1/2, and 3/2. The signal of $I=0$ spin mercury appears in the field very close to the free spin. Due to the very large magnitude of A, the hyperfine constant and the limited range of the field sweep of the ESR spectrometer used, all the components of the hyperfine lines have not been recorded at X-band frequency as seen in Fig. 4, but they are measurable at K-band frequency as shown in Fig. 5. The center of the hyperfine lines does not refer to the true g-value for Hg(I) because the quantization axis of the electron spin differs from the applied magnetic field.

The K-band spectrum of powder gives the whole hyperfine spectrum and allows calculation of all prin-

13) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals.," Elsevier Publishing Co., Amsterdam (1967), p. 236.

cipal values. With respect to the hyperfine spectrum of Hg(I), due to its large hyperfine splitting the difference in intensity of the hyperfine lines is distinctly observed. This is interpreted by the fact that the transition moment is a function of the magnetic field at which the signal appears. From the whole structure of the spectrum of the powdered sample and the number of isotopes it is concluded that the number of species of the hot ion of Hg(I) is one and the structure of its crystal field is slightly deviated from axial symmetry.

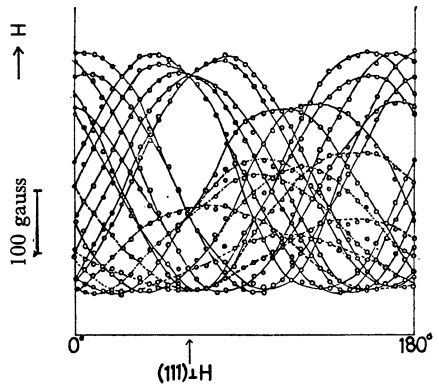

Fig. 11. Angular dependence of hyperfine structure line of γ-irradiated single crystal of $K_2[Hg(CN)_4]$ with the rotation with $[0\bar{1}1]\perp H$.
The second line of ^{199}Hg hyperfine structure is shown. (X-band)

The number of sites and the orientation of Hg(I) complex have been determined from X-band single crystal spectra. For examination of the spectrum, the lines of ^{199}Hg are chosen as an example. The result of the rotation of the γ-irradiated single crystal of $K_2[Hg(CN)_4]$ with the $[0\bar{1}1]$ axis perpendicular to the static magnetic field is shown in Fig. 11. When the [111] axis is parallel to the static magnetic field, the spectrum is the simplest consisting of four lines. The one in the highest field is assumed to refer to Hg(I) in the site of Hg(II)–CN along the [111] axis. With the variation of the angle, the line begins to be separated into six lines. The largest splitting does not occur at the angle where Hg(II)–CN of the host lattice is parallel to the magnetic field, but occurs at the angle about 20° deviated from the direction of Hg(II)–CN. At an interval of the tetrahedral angle, six lines similarly appear in the higher field which are assumed to refer to the sites corresponding to Hg(II)–CN along $[1\bar{1}\bar{1}]$. The other nine lines are assigned to those resulting from the sites corresponding to the remaining two Hg(II)–CN directions $[\bar{1}\bar{1}1]$ and $[\bar{1}1\bar{1}]$. With this rotation, $[\bar{1}\bar{1}1]$ and $[\bar{1}1\bar{1}]$ are equivalent, which makes the number of lines smaller than twelve (6×2).

From the results we reach the following conclusion. The reduction is accompanied by the distortion of the mother lattice of the complex to some extent. The symmetry of Hg(I) complex is not far from the axial symmetry of the diamagnetic compound with a structure slightly distorted from C_{3v}. The distortion occurs nearly parallel to the Hg(II)–CN bonding and the deviation is estimated to be about 20°. Six directions of the distortion are distributed around each Hg(II)–CN direction, probably with the distribution determined by the arrangement of the neighboring atoms. The number of sites is twenty-four (6×4). The Hg(I) complex is orientated to a direction slightly deviated from Hg(II)–CN bonding in the host lattice.

The parameters of ESR hyperfine spectrum are calculated from the K-band powder spectrum by Eq. (1). For the sake of simplification, approximation by means of the equation for the strong allowed transition under the conditions of axial symmetry was adopted. Equations for ^{199}Hg ($I=1/2$) are (4) and (5). The equations for $S=1/2$ and $I=3/2$ are found in literature[14] and quoted for ^{201}Hg ($I=3/2$):
For the symmetry axis parallel to H, we have

$$\begin{aligned}
h\nu &= \frac{1}{2}g_{//}\beta H_1 + A + \frac{1}{2}[(g_{//}\beta H_1 + A)^2 + 3B^2]^{1/2} \\
h\nu &= \frac{1}{2}[(g_{//}\beta H_2 + A)^2 + 3B^2]^{1/2} + \frac{1}{2}[(g_{//}\beta H_2)^2 + 4B^2]^{1/2} \\
h\nu &= \frac{1}{2}[(g_{//}\beta H_3 - A)^2 + 3B^2]^{1/2} + \frac{1}{2}[(g_{//}\beta H_3) + 4B^2]^{1/2} \\
h\nu &= \frac{1}{2}g_{//}\beta H_4 - A + \frac{1}{2}[(g_{//}\beta H_4 - A)^2 + 3B^2]^{1/2}
\end{aligned} \tag{6}$$

For the symmetry axis perpendicular to H, we have

$$\begin{aligned}
h\nu &= \frac{1}{2}g_{\perp}\beta H_1 + B + \frac{1}{2}\left[(g_{\perp}\beta H_1 + B)^2 + 3\left(\frac{A+B}{2}\right)^2\right]^{1/2} \\
h\nu &= \frac{1}{2}\left[(g_{\perp}\beta H_2 + B)^2 + 3\left(\frac{A+B}{2}\right)^2\right]^{1/2} + \\
&\qquad \frac{1}{2}\left[(g_{\perp}\beta H_2)^2 + 4\left(\frac{A+B}{2}\right)^2\right]^{1/2} \\
h\nu &= \frac{1}{2}\left[(g_{\perp}\beta H_3 - B)^2 + 3\left(\frac{A+B}{2}\right)^2\right]^{1/2} + \\
&\qquad \frac{1}{2}\left[(g_{\perp}\beta H_3)^2 + 4\left(\frac{A+B}{2}\right)^2\right]^{1/2} \\
h\nu &= \frac{1}{2}g_{\perp}\beta H_4 - B + \frac{1}{2}\left[(g_{\perp}\beta H_4 - B)^2 + 3\left(\frac{A+B}{2}\right)^2\right]^{1/2}
\end{aligned} \tag{7}$$

Calculations were repeated following the method adopted for Cd(I) from the observed separation of members. First, from the observed magnetic field values for z-direction and x-direction in the powder spectrum, principal values for z-direction and x-direction were calculated under the assumption of the axial symmetry. The principal values for y-direction were calculated next. The results are:

For ^{199}Hg ($I=1/2$)

$g_{zz}=1.97\pm0.05$	$A_{zz}=(5.02\pm0.05)\times10^3$ gauss
$g_{yy}=1.96\pm0.05$	$A_{yy}=(4.58\pm0.00)\times10^3$ gauss
$g_{xx}=1.96\pm0.05$	$A_{xx}=(4.56\pm0.05)\times10^3$ gauss

and for ^{201}Hg ($I=3/2$)

$g_{zz}=1.97\pm0.05$	$A_{zz}=(1.85\pm0.01)\times10^3$ gauss
$g_{yy}=1.96\pm0.05$	$A_{yy}=(1.68\pm0.02)\times10^3$ gauss
$g_{xx}=1.96\pm0.05$	$A_{xx}=(1.66\pm0.02)\times10^3$ gauss

(4) Comparison of the Results for M(I) Complexes. The analysis of ESR spectrum shows that hot ion of paramagnetic M(I) is produced by γ-ray irradiation of M(II) complex compounds, where M(I) ion is trapped in the host lattice of M(II) compound with a small distortion. The concentration of M(I) ion is

14) W. C. Lin and C. A. McDowell, *Mol. Phys.*, **7**, 223 (1964).

evaluated to be less than about 10^{-1} % by measurement of the intensity of the ESR signal of M(I).

When M(II) is reduced to M(I) by γ-rays, the symmetry of M(II) is also reduced from T_d to C_{3v}. In the case of cyanomercurate(I) in cyanomercurate(II), the symmetry is more distorted than C_{3v}. However, even in this case, the deviation from C_{3v} is small. The symmetry around M(I) is not C_∞ but C_{3v}. We assume the product to be assigned to $[M(I)(CN)_4]^{3-}$ and not to $[M(I)(CN)_3]^{2-}$, because we consider it difficult to eliminate one cyano radical from the sphere of complex.

Details of the characteristic difference of Zn(I), Cd(I), and Hg(I) are as follows. In Zn(I), one of the four Zn–CN bondings is stretched with equal probability of stretching for four bondings. Hence, the irradiation product Zn(I) is one species with four equivalent sites of electron. In the case of Cd(I), stretching similar to that in Zn(I) occurs along four Cd–CN bondings equivalently. However, in the former, four different kinds of stretching occur along one bonding, which results in possible 16 sites (4 species $\times$ 4 bondings) of electron, all with C_{3v} symmetry. In Hg(I), electron is not sited along any one of Hg(II)–CN bondings, but at a place slightly apart from the bonding. Six different sites are referred to for one Hg(II)–CN direction from the pattern of the spectra. The number of possible sites of the electron is 24.

The electronic structure of the product is also of interest. The values of $|\Psi(0)|^2$ and $\langle r^{-3}\rangle$ for the M(I) ions have not been determined qualitatively. We can evaluate the hyperfine splitting constants for $(n+1)s$ orbital electron with the use of the data of isoelectronic Cu, Ag, and Au atoms using Goudsmit's relation $z_i z_0^2 \propto |\Psi(0)|^2$ [15] and the value of the nuclear gyromagnetic ratio. In the case of Cd(I), the reported data of the Cd(I) ions isolated in argon matrix at 4.2°K is available.[9] It gives the isotropic hyperfine splitting constants, $A=(5137\pm1)$ gauss for ^{111}Cd(I) and $A=(5347\pm1)$ gauss for ^{113}Cd(I). In our experiment, Cd(I) complex has axial symmetry and the hyperfine splitting is divided into the isotropic and anisotropic parts. The ratio of the hyperfine splitting constants of the two nuclei ^{111}Cd and ^{113}Cd agrees with the ratio of the nuclear gyromagnetic ratio within experimental error. The isotropic parts of the observed hyperfine splitting constants leads to the spin population of $5s$ orbital of 0.24 for species C and 0.28 for species A. Taking the anisotropic part of the hyperfine splitting constant into consideration, the hybridization for the unpaired electron orbital is taken to be between sp^2 and sp^3. The same statement might hold for the electronic structure of Hg(I) complex from the estimated hyperfine splitting constants. This supports the assumed symmetry of C_{3v}. We assume further that the complexes of Cd(I) and Hg(I) do not differ so much from each other with respect to the electron densities. This agrees with the observed result after normalization by nuclear gyromagnetic ratio. In contrast to the case of Cd(I) and Hg(I), the observed hyperfine splitting of Zn(I) complex is considerably small, suggesting that the unpaired electron density on zinc nucleus is small and the electron is delocalized considerably to the ligand atoms.

The remarkable difference between the M(I) complexes lies in the stability of the oxidation number, (I). First, the sequence of the signal intensity under the same γ-ray dose is Hg(I)>Cd(I)>Zn(I). Second, Zn(I) and three species of Cd(I) decay at 77°K and species A of Cd(I) and Hg(I) are stable at this temperature. It should be noted that of the Cd(I) species those which decay at 77°K have smaller hyperfine splitting constant than the stable one.

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Note Added in Proof. We have recently noticed that M. C. R. Symons and J. K. Yardell have measured the ESR of Hg(I) (*J. Chem. Soc.*, *A*, **1971**, 761). However, they only report the production of Hg(I) in the γ-irradiated frozen solutions.

15) S. Goudsmit, *Phys. Rev.*, **43**, 636 (1933).