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ESR Study of Hot Ions : Pb(III) in γ-Irradiated Lead Tetraacetate

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An unstable paramagnetic Pb(III) hot ion was identified in γ-irradiated polycrystalline lead tetraacetate by ESR hyperfine spectrum of ^{207}Pb isotope. ESR parameters are as follows: $(g_x, g_y, g_z)=(2.0063, 2.0077, 2.0035)$. $(A_x/g_x\beta, A_y/g_y\beta, A_z/g_z\beta)$ =(12819, 12827, 12854 (gauss)).

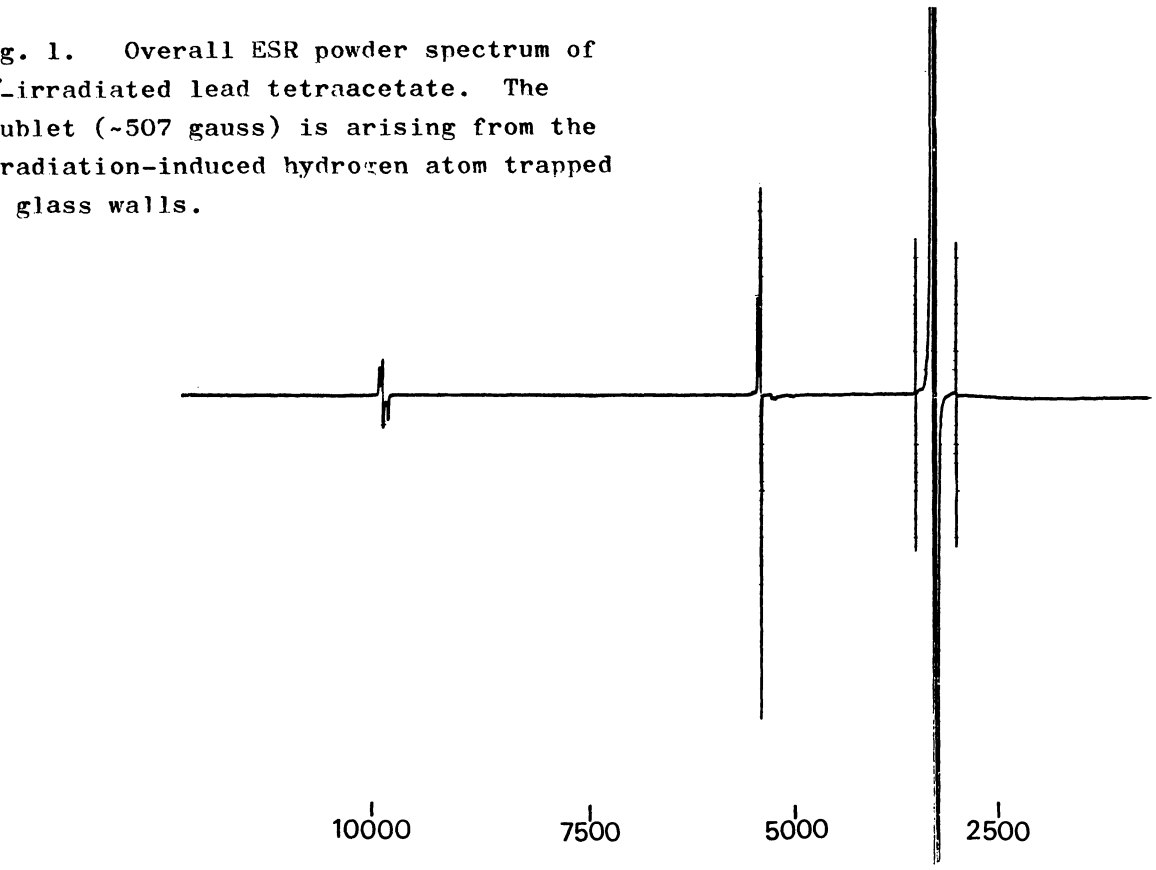
We wish to report here that we have found recently the formation of Pb(III) hot ions in γ-irradiated lead tetraacetate, $Pb(CH_3COO)_4$ by the detection of ESR hyperfine spectrum due to ^{207}Pb.

Lead tetraacetate was obtained from Wako Pure Chemicals and was recrystallized from glacial acetic acid. The powdered sample was degassed in a quartz tube at 10^{-3} mmHg and sealed in vacuum. ^{60}Co γ-ray irradiation was carried out at 77°K to a total dose of 1×10^6 rad. The ESR spectra were recorded at 77°K on a JEOL 3BS X-band spectrometer by using 100 kHz modulation of the magnetic field. The magnetic field strength was measured by ^1H and ^7Li NMR. The color of the sample was rendered orange on exposure to γ-rays. Taking out from liquid nitrogen Dewar, this color diminished rapidly accompanying the disappearance of the ESR signals assigned to Pb(III) complex.

The powder ESR spectrum of γ-irradiated lead tetraacetate is shown in Fig. 1. There coexist the irradiation-induced ESR signals from the glass walls which are due to the glass defects, and the lines of hyperfine structure of atomic hydrogen. The spectrum of -irradiated lead tetraacetate consists of the signals of radicals originated from the ligand and those of Pb(III) complex.

Pb(III) ion is a $^2S(1/2)$ state with $5d^{10}6s^1$ electronic configuration. The line at ~5450 gauss is assigned to $(F = 1, m_F = -1)\leftrightarrow(F = 1, m_F = 0)$ transition of 21.6 % abundant ^{207}Pb isotope ($I = 1/2$), which corresponds to the high field component of the doublet. Because the hyperfine interaction constant, A, is so large, the electron and nuclear spins are strongly coupled ($F = S + I$) and (F, m_F) are good quantum numbers. At X-band frequency, the microwave energy is smaller than A, and the another component of the doublet $(F = 0, m_F = 0) \leftrightarrow (F = 1, m_F = +1)$ is unobservable. The second hyperfine line $(F = 1, m_F = 0)\leftrightarrow (F = 1, m_F = +1)$ transition, was observed at ~10000 gauss, which would be forbidden in the strong field limit ($A\ll g\beta H$). The anisotropic line-shape is clearly seen with respect to the high field line as the Zeeman term ($g\beta H$) is more dominant in the latter. The lines arising from lead isotopes with zero nuclear spin could not be distinguished from those of radicals.

Fig. 1. Overall ESR powder spectrum of γ-irradiated lead tetraacetate. The doublet (~507 gauss) is arising from the irradiation-induced hydrogen atom trapped in glass walls.



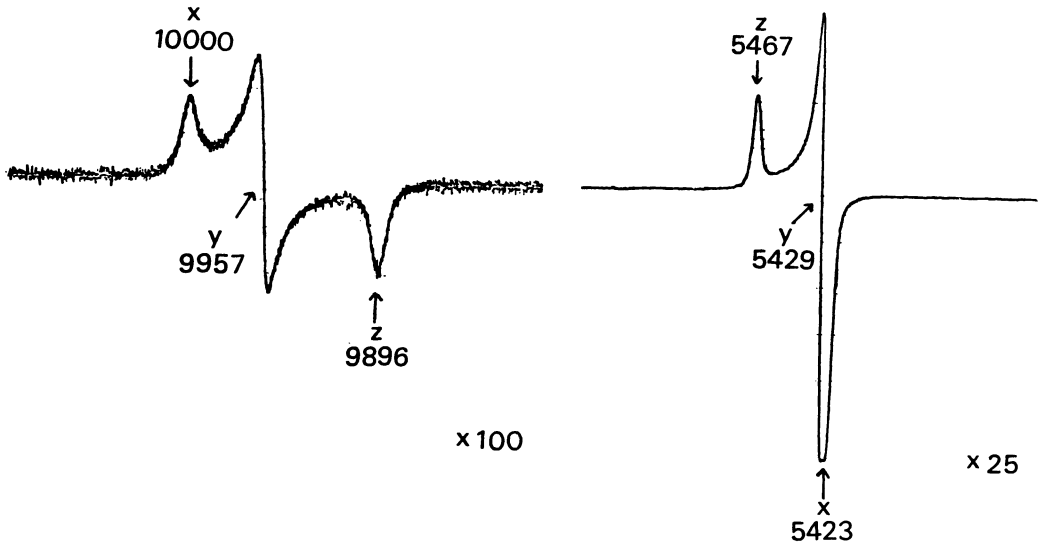


Fig. 2. Hyperfine components of $^{207}Pb(III)$ in ESR powder spectrum of γ-irradiated lead tetraacetate. In the low field is (F = 1, m_F = -1) ↔ (F = 1, m_F = -1) transition, and in the high field is (F = 1, m_F = 0) ↔ (F = 1, m_F = +1) transition. The microwave frequency was 9187.2 MHz.

The following spin Hamiltonian may be taken for the interpretation of the observed result where for ^{207}Pb I = S = 1/2.

$$\mathcal{H} = H \cdot G \cdot S + S \cdot A \cdot I$$

The parameters for ^{207}Pb(III) in γ-irradiated lead tetraacetate calculated by the method shown in Appendix are

$$g_x = 2.0063 \pm 0.0010 \qquad A_x/g_x\beta = 12819 \pm 10 \text{ gauss}$$
$$g_y = 2.0077 \pm 0.0010 \qquad A_y/g_y\beta = 12827 \pm 10 \text{ gauss}$$
$$g_z = 2.0035 \pm 0.0010 \qquad A_z/g_z\beta = 12854 \pm 10 \text{ gauss}$$

The fields for principal axes, x, y, z of G- and A-tensors were assigned as shown in Fig. 2.

For the case of free ion, hyperfine splitting constant for $5d^{10}6s^1$ of Pb(III) has been measured with a value[1)]

$$A_{6s} = 2.60 \pm 0.05 \text{ cm}^{-1}$$

The hyperfine splitting constant for Pb(III) in γ-irradiated lead tetraacetate is about 46 % of the free ion, ($A_x = 1.2007 \pm 0.0010$ cm^{-1}, $A_y = 1.2023 \pm 0.0010$ cm^{-1}, $A_z = 1.2023 \pm 0.0010$ cm^{-1}). The reduction of A can be attributed to the delocalization of electron to the surrounding ligand atoms. X-ray structure analysis shows that the oxygen atoms of four acetate ions constitute a flattened trigonal dodecahedron around a lead atom.[2)] The smallness of the anisotropy of A-tensor suggests that this structure of the mother complex is not heavily destroyed in the Pb(III) complex. It has been reported so far that unstable metal complexes can be formed by irradiation of inorganic complexes by γ-ray or X-ray where the central metal ions have a different oxidation state from the mother complexes.[3-7)] These ions have been referred to by Fujiwara as hot ions.[6)] Hot ions are unstable especially in the sense that the crystal field of the mother complex is maintained although the oxidation state is changed. Pb(III) complex in γ-irradiated lead tetraacetate is considered as an example of hot ions.

It has been reported in the literature that Pb(III) is formed in the host lattices of ZnTe[8)], ZnSe[9)], ZnO[10)], KCl[11)], $CaCO_3$[12)], $CaWO_4$[13)], ThO_2[14)] and CdS[15)], when lattice defect hole is trapped by Pb(II) which is doped in the lattice as the substitutional impurities. ESR spectra of Pb(III) were also observed in γ-irradiated lead carbonate and γ-irradiated frozen solution of lead nitrate.[15)] In our work, Pb(IV) trapped an electron forming Pb(III) during irradiation. Moreover, sharp features of ESR spectrum enabled to reveal a small anisotropy of G- and A-tensors.

Appendix

In the case that the hyperfine field is so large, the high field approximation is not sufficiently used. When the principal axes of the G- and A-tensors are parallel and the magnetic field is parallel to one of the axes, the Hamiltonian, $\mathcal{H}$, is exactly solved. (for ^{207}Pb(III), S = I = 1/2)

$$\mathcal{H} = H \cdot G \cdot S + S \cdot A \cdot I$$

The transitions under experimental conditions for the case of H along the principal axes are given respectively with the principal values, g_x, g_y, g_z, A_x, A_y, A_z. $(F = 1, m_F = -1) \leftrightarrow (F = 1, m_F = 0)$ transitions are

$$\text{for } H/\!/x \quad h\nu = -\frac{A_x}{2} + \frac{1}{4}\{(2g_x\beta H)^2 + (A_y + A_z)^2\}^{1/2} + \frac{1}{4}\{(2g_x\beta H)^2 + (A_y - A_z)^2\}^{1/2}$$

$$\text{for } H/\!/y \quad h\nu = -\frac{A_y}{2} + \frac{1}{4}\{(2g_y\beta H)^2 + (A_z + A_x)^2\}^{1/2} + \frac{1}{4}\{(2g_y\beta H)^2 + (A_z - A_x)^2\}^{1/2}$$

$$\text{for } H/\!/z \quad h\nu = -\frac{A_z}{2} + \frac{1}{4}\{(2g_z\beta H)^2 + (A_x + A_y)^2\}^{1/2} + \frac{1}{4}\{(2g_z\beta H)^2 + (A_x - A_y)^2\}^{1/2}$$

$(F = 1, m_F = 0) \leftrightarrow (F = 1, m_F = +1)$ transitions are

$$\text{for } H/\!/x \quad h\nu = \frac{A_x}{2} + \frac{1}{4}\{(2g_x\beta H)^2 + (A_y - A_z)^2\}^{1/2} - \frac{1}{4}\{(2g_x\beta H)^2 + (A_y + A_z)^2\}^{1/2}$$

$$\text{for } H/\!/y \quad h\nu = \frac{A_y}{2} + \frac{1}{4}\{(2g_y\beta H)^2 + (A_z - A_x)^2\}^{1/2} - \frac{1}{4}\{(2g_y\beta H)^2 + (A_z + A_x)^2\}^{1/2}$$

$$\text{for } H/\!/z \quad h\nu = \frac{A_z}{2} + \frac{1}{4}\{(2g_z\beta H)^2 + (A_x - A_y)^2\}^{1/2} - \frac{1}{4}\{(2g_z\beta H)^2 + (A_x + A_y)^2\}^{1/2}$$

Using above equations, the parameters were calculated from the observed values of the magnetic field. First, combining the equations, ν, g_x, g_y and g_z are eliminated. Starting from the $A_x/g_x\beta$, $A_y/g_y\beta$, $A_z/g_z\beta$ values chosen appropriately, more adequate $A_x/g_x\beta$, $A_y/g_y\beta$, $A_z/g_z\beta$ values were calculated. Calculations were repeated to converge by computer. Then, g_x, g_y and g_z were calculated from those obtained values.

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