Electron Paramagnetic Resonance Study of γ-Ray Irradiated Phosphate Glasses*

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In the last few years considerable progress has been made in acquiring knowledge about network defects in the glassy state by using paramagnetic resonance measurements.

Paramagnetism due both to defects produced in the lattice and to the presence of impurity atoms has been observed in irradiated quartz,(1) some silicate glasses(2) and alkali borate glasses.(3) Typical paramagnetic centers ascribed hitherto in silicate or borate glasses are an electron trapped at an oxygen vacancy, an electron trapped in the alkali ion, and a hole trapped at an oxygen ion. The paramagnetic centers described as impurity centers are a hole trapped on a bridging oxygen which is bonded to a substitutional Al^- ion for silica in the silicon oxide, and an electron trapped in an interstitial hydrogen atom in a glass network.

The phosphate glasses become strongly colored under γ-ray irradiation. The most sensitive glass for irradiation is silver-activated phosphate glass. The phosphate glasses offer a simple and precise method of measuring gamma-ray doses with a commercial densitometer or a spectrophotometer.

The EPR study of the defect centers in irradiated glass containing phosphorus was first reported by Karapetyan and Yudin.(4) They observed an EPR spectra consisting of a two-line structure at $g=2.0038$. This two-line structure was attributed to hyperfine interaction with a ^{31}P nucleus.

In the present investigation, it has been found that there are three distinct types of defect centers in irradiated phosphate glasses. These paramagnetic centers seem to be connected with the peculiar structure of phosphate glass.

The basic structure of phosphate glass, which consists of sp^3 orbitals with an unsymmetric PO_4 tetrahedron, shows a considerable π-bond character.(5) The structure of such multiply-bonded glass is different from that of the silicate or borate glasses. Moreover, the compositions of the phosphate glasses have ratios of " modifier " oxide to phosphorus(V) oxide between one and three. In contrast, the silicate or borate glasses usually investigated have such compositions that this ratio is less than one.

In the present study, the relation between defect centers and the composition of phosphate glass will be discussed.

Experimental

The EPR spectra were obtained by using a Varian Model 4501 EPR spectrometer at a microwave frequency of 9.4 kMc./sec. operating with a 100 kc./sec. field modulation. The EPR data presented in this study were obtained at room temperature.

The hyperfine structure of an alcoholic dilute solution of manganese(II) chloride was used as a standard for the magnetic field, and DPPH, for the g-value. Powder or glassy samples were enclosed in evacuated glass tubes during the γ-ray irradiation and the measurements.

The composition of alkaline phosphate glasses was $x\%M_2O(100-x)\%P_2O_5$ [M=Li, Na, K], where $M/P=1.5$ and 2.0, while that of alkaline earth phosphate glasses was $x\%RO(100-x)\%P_2O$ [R=Ca, Ba], where $R/P=0.5$ and 1.0 (in this paper weight percentages are used). These samples were melted in a platinum crucible at about 1100—1400°C. Metaalkaline phosphate glass was made from (MPO_3), where M=Li, Na. The composition of the alumino alkaline phosphate glasses used in this investigation was $50\%LiPO_3$ - $50\%AlPO_3$ and $80\%LiPO_3$ - $20\%AlPO_3$.

Samples of condensed phosphate were prepared by the dehydration of $(RH_{1-2}PO_4)$ [R=Li, Na, K, Ca or Ba] at an elevated temperature, usually in the 500—800°C range.

The samples were irradiated at room temperature with ^{60}Co rays (5—6×10^6 r.).

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* Preliminary communication,: This Bulletin, **37**, 1087 (1964).

1) R. A. Weeks, *J. Appl. Phys.*, **27**, 1376 (1956); J. H. E. Griffith, J. Owen and I. M. Ward, Report of the Conference on Defects in Crystalline Solids, p. 81 (1955), London, Physical Society; M. C. M. O'Brien, *Proc. Roy. Soc.*, **A231**, 404 (1955).

2) J. S. van Wieringen andA. Kats, *Philips Res. Rep.*, **12**, 432 (1957); C. M. Nelson and R. A. Weeks, *J. Am. Ceram. Soc.*, **43**, 399 (1960); S. Lee and P. J. Bray, *Phys. Chem. Glass*, **3**, 37 (1962).

3) Y. Nakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1629 (1961); Y. Nakai, *Zeits, f. Phyik. Chem.*, in press; S. Lee and P. J. Bray, *J. Chem. Phys.*, **39**, 2863 (1963).

4) G. O. Karapetyan, D. M. Yudin, *Soviet Phys. Solid State*, **3**, 2063 (1963).

5) J. R. van Vazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York (1958).

Results

Before irradiation no paramagnetic resonance was found on any sample, but after irradiation all of them showed resonance and were purple or pink rose.

Figures 1 and 2 shows the EPR spectra of irradiated alkaline or alkaline-earth phosphate glasses. In the case of a sodium or potassium phosphate glass, the peaks of P_a and P_b disappear, leaving only two central peaks, P_{c1} and P_{c2}. No spectra were observed from the sample of $(KPO)_3$-condensed phosphate irradiated with γ-rays (5×10^6 r.).

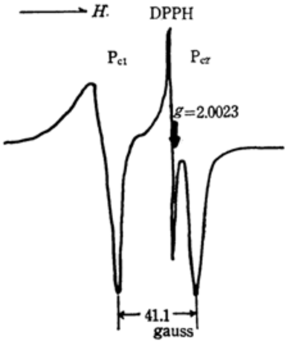

Fig. 1. The EPR spectrum obtained for γ-ray irradiated alkaline or alkaline earth phosphate glass.

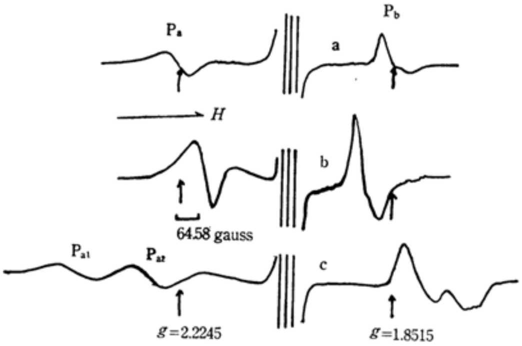

Fig. 2. The EPR spectra in low and high magnetic fields obtained for γ-ray irradiated phosphate glasses. The central lines are the spectra due to the phosphorus center shown in Fig. 1.

a) $LiPO_3$ glass
b) 10% $BaCO_3$ - 90% $LiPO_3$ glass
c) 41.3% $CaCO_3$ - 49.7% P_2O_5 glass

The *g*-values of the derivative peaks denoted P_{c1} and P_{c2} are independent of the kind of alkaline or alkaline earth modifier incorporated. These correspond to those reported by Karapetyan and Yudin.[4] The *g*-value at the center of these two peaks is measured as 2.0058. The distance between the derivative peaks, P_{c1} and P_{c2}, is 41.1 gauss.

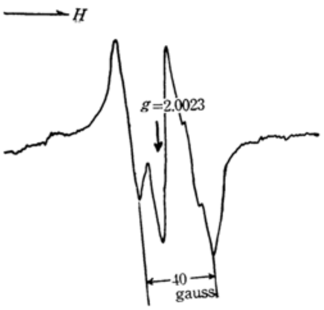

Fig. 3. The EPR spectrum obtained for γ-ray irradiated $(LiPO_3)_n$ condensed phosphate.

Figure 3 shows the EPR spectrum obtained from the irradiated condensed phosphate from which $LiPO_3$ glass was made. As a result, the difference between $LiPO_3$ glass and $LiPO_3$ condensed phosphate was found.

The intensity of the two-line structure, P_{c1} and P_{c2}, can easily be reduced by heating it at 130—160°C. The fading speed by the thermal treatment is dependent on the kind of alkaline or alkalin-earth modifiers. The resistance to thermal bleaching increases in the order $Ca\approx Ba<Li<Na<K$. Moreover, the fading speed is dependent on the $R=M/P$ ratio. As the ratio ranges from three to one, the fading speed shows a tendency gradually to become slower. The two-line structure has the same response to both thermal annealing and optical annealing.

In addition to the two-line structure, the observed spectra appear to display other two weak absorption lines, P_a and P_b, on the low and high magnetic field sides. Figure 2 shows that the position and the width of the anisotropic resonances, P_a and P_b, depend greatly upon the type of alkaline or alkaline-earth ions.

The position and the width of two weak resonances in lithium phosphate glasses contaminated with calcium or barium are different from those exhibited in pure lithium phosphate glass, but the shape may be substantially the same, as Figs. 2a and 2b show.

It appears that the relative intensity of the two weak peaks increases in the order $Li<Ba\approx Ca$. Moreover, a relation exists between the radiation-induced paramagnetic intensity and the constitution of glass. As the proportion of the network-modifying atom increases in glasses, the relative intensity greatly increases. We have found that the two weak peaks are completely removed by annealing them at 380—450°C for 30 min.

It is remarkable that the derivative curve on the low magnetic field side obtained from alkaline-earth phosphate glasses consists of

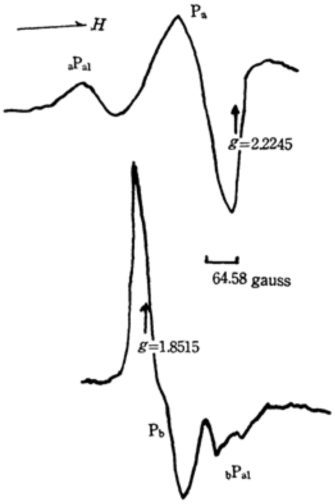

Fig. 4. The EPR spectrum obtained for γ-ray irradiated alumino phosphate glass of composition 50% $Al(PO_3)_3$ - 50% $LiPO_3$.

two peaks, as is shown in Fig. 2c. The fading speed of P_{a1} to the thermal annealing may be a little more rapid than that of P_{a2}.

In phosphate glasses modified with such an ion as calcium, barium or lithium, the two weak resonances, P_a and P_b, seem to appear easily.

Alumino alkaline phosphate glasses irradiated with γ-rays exhibit the same two-line structure, P_{c1} and P_{c2} as that displayed in $LiPO_3$ glass. The EPR intensity of the outer side peaks, $_aP_{a1}$ and $_bP_{a1}$, increases in proportion to the Al_2O_3 content of the $LiPO_3$ glass. However, as Fig. 4 shows, the shapes of the P_a and P_b centers are independent of the Al_2O_3 content.

Discussion

Alkali or Alkaline-earth Phosphate Glasses. —The irradiated phosphate glasses exhibit the EPR spectra of two strong lines (P_{c1} and P_{c2}) and of the other two weak absorption lines. One of the weak absorption lines appears to display a broad derivative peak on the low magnetic field side ($g=2.2245$), and the other, a broad asymmetric derivative peak on the high magnetic field side ($g=1.8575$). The former is denoted by P_a, and the latter, by P_b.

P_c Center.—Two peaks (P_{c1} and P_{c2}) in the derivative curve have the same response in the thermal annealing and optical bleaching, and this structure is independent of the kind of alkaline modifier and of the isotopic substitution of hydrogen. These facts suggest that the two lines arise from only one type of paramagnetic center, and so the magnetic hyperfine structure of two peaks may be ascribed to ^{31}P with $I=1/2$.

The observed g-value of the two-line structure shown in Fig. 1, which is larger than that of a free electron, suggests that the paramagnetic center is a trapped hole produced in the glass network by irradiation.

In order to analyze the observed two-line structure in terms of the hyperfine interaction of an unpaired spin, $S=1/2$, with a ^{31}P nucleus, it is assumed that the phosphorus center experiences a crystalline field whose symmetry is axial. If the crystalline electric field experienced by the phosphorus center were spherically symmetric or lower than axial, the shape of the derivative curve would be symmetrical or more complicated.

The spin resonance of the (PO_4) defect can be described in terms of the following spin Hamiltonian:⁶⁾

$$\mathscr{H}=\beta[g_{\parallel} S_z H_z+g_{\perp}(S_x H_x+S_y H_y)] + A S_z I_z + B(S_x I_x+S_y I_y) \qquad (1)$$

where $g_{\parallel}$ and $g_{\perp}$ are the g factors along and at right angles to the z direction, while A and B are the hyperfine interaction parameters of the ^{31}P nuclei. The ^{31}P nuclei ($I=1/2$) have no quadrupole moment, and the diple-dipole interaction of neighboring centers is neglected in order to simplify the analysis of the observed hyperfine structure.

In the case of a glassy or powdered substance, θ takes random values, and the hyperfine structure is the envelope of the properly-weighted spectra obtained in simple crystals at all possible orientations.

According to the theoretical calculation,⁷⁾ the shape of the glassy spectrum, $g(H)$, is the sum of the line shape functions of $2I+1$ components as follows:

$$g(H)=\sum_{M=-I}^{I} g_M(H)$$

where $$g_M(H)=\frac{No}{2}\sin\theta\frac{d\theta}{dH}$$

The first-order hyperfine resonance condition given by the spin Hamiltonian is shown as follows:⁶⁾

$$H=\frac{h\nu_0}{\beta}(g^2{}_{\parallel}\cos^2\theta+g^2{}_{\perp}\sin^2\theta)^{-1/2} -\frac{M}{\beta}(A^2 g^2{}_{\parallel}\cos^2\theta+B^2 g^2{}_{\perp}\sin^2\theta)^{1/2} \times(g^2{}_{\parallel}\cos^2\theta+g^2{}_{\perp}\sin^2\theta)^{-1} \qquad (3)$$

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6) B. Bleaney, *Phil. Mag.*, 42, 441 (1951).

7) R. H. Sands, *Phys. Rev.*, 99, 1222 (1955); S. M. Blinder, *J. Chem. Phys.*, 33, 748 (1960); R. Neiman and D. Kivelson, ibid., 35, 156 (1961).

Differentiating 3 with respect to θ, and substituting $d\theta/dH$ in 3, we find the glassy spectrum, $g(H)$.

From the present measurements of the phosphorus center, P_c, which gives rise to the two-line hyperfine structure observed at the X-band frequency, we find

$$S=\frac{1}{2}, \qquad I=\frac{1}{2}$$

$$g_{\parallel}=2.0243, \quad g_{\perp}=2.0058$$

$$|A|=3.81\times10^{-3}\,\mathrm{cm}^{-1}, \quad |B|=3.75\times10^{-3}\,\mathrm{cm}^{-1}$$

This result is consistent with the two-line hyperfine structure observed in the irradiated phosphate glasses and shown in Fig. 5.

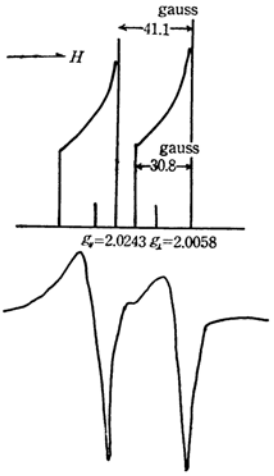

Fig. 5. Comparison between the hyperfine structure contructed from the spin Hamiltonian of Eq. 1 for the case of X-band frequency and the first derivative obtained for γ-ray irradiated phosphate glass.

As models for this resonance, two possibilities were considered: (1) a hole trapped on a singly-bonded oxygen, and (2) a hole trapped on the phosphorus atom in the PO_4 unit.

The wave function of the hole is assumed to occupy an orbital:

$$\Psi=\eta_P\phi_P+\eta_O\phi_O \tag{4}$$

where ϕ_O and ϕ_P are hybrid orbitals on singly-bonded oxygen and phosphorus respectively. The coefficients are subjected to the normalizing requirements:

$$\eta^2{}_P+\eta^2{}_O+2\eta_O\eta_P S=1$$

where S is the overlap, $\int\phi_P\phi_O d\tau$.

The hybrid orbital on phosphorus, ϕ_P, is considered to consist mainly of a tetrahedral bonding orbital of the form $[(1/2)(|3s\rangle+\sqrt{3}\,|3p\rangle)]$, where $|3s\rangle$ and $|3p\rangle$ are the 3s and 3p orbitals of the phosphous that are used in the P—O covalent bonding. After γ-ray irradiation, the configuration of the PO_4 structure assumed to remain tetrahedral.

The hyperfine interaction parameters, A and B, of the molecular orbital 4 with the phosphorus nucleus are related to the contact and the dipolar interaction by:[8]

$$A=\frac{1}{4}g\beta\left(\frac{\mu}{I}\right)\left[\frac{8\pi}{3}|\varphi_{3s}(0)|^2{}_P+\frac{12}{5}\langle r^{-3}\rangle_{3p,P}\right]\eta^2{}_P$$

$$B=\frac{1}{4}g\beta\left(\frac{\mu}{I}\right)\left[\frac{8\pi}{3}|\varphi_{3s}(0)|^2{}_P-\frac{6}{5}\langle r^{-3}\rangle_{3p,P}\right]\eta^2{}_P$$

where $\varphi_{3s}(0)$ denotes the wave function of the unpaired electron evaluated at the phosphorus, and $\langle r^{-3}\rangle$ is the average for the 3p orbital about the phosphorus atom.

Mayers[9] has performed a SCF treatment of the ground state phosphorus atom, and for his wave function the 3s orbital has $(8\pi/3)\times|\varphi_{3s}(0)|^2=46.93$ a. u. Similarly, Mayer's wave function gives, for the 3p orbital, $\langle r^{-3}\rangle=3.34$ a. u.

Therefore, it is possible to evaluate the hyperfine parameters of the ground-state phosphorus atom. We find that the isotropic part, $(8\pi/3)g\beta(\mu/I)|\varphi_{3s}(0)|^2$, is $0.33\,\mathrm{cm}^{-1}$; the anisotropic part, $(6/5)g\beta\times(\mu/I)\langle r^{-3}\rangle_{3p,P}$, is $2.86\times10^{-2}\,\mathrm{cm}^{-1}$, and the calculated values of the hyperfine interaction parameter, $A/\eta^2{}_P$ and $B/\eta^2{}_P$, are $96.8\times10^{-3}\,\mathrm{cm}^{-1}$ and $75.3\times10^{-3}\,\mathrm{cm}^{-1}$ respectively.

By comparing the experimental data and the calculated values of the hyperfine interaction parameters, we find $\eta_P=0.2$.

It can be seen, thus, that the experimental data obtained for the phosphorus center suggest that the hole interacting with a P nucleus is only weakly associated with the phosphorus atom. Perhaps the phosphorus center consists mainly of a hole trapped at a singly-bonded oxygen atom in the PO_4 unit, and the hole would spend 95—96% of its time on the oxygen and 4—5% of its time on the phosphorus atom.

The material from which $LiPO_3$ glass was made was subjected to γ-ray irradiation at room temperature. After irradiation, the spectrum shown in Fig. 3 was observed. In spite of its having the same composition, however, the position and also the shape of the EPR spectrum in the glassy state are different from those of the condensed phosphate. However, the EPR spectrum of the phosphorus center obtained at room temperature from the irradiated $(NaPO_3)_3$ of a ring structure was the same as those obtained from irradiated phosphate glasses. In the

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[8] See, for example, A. R. Reinberg, *J. Phys. Chem.*, **41**, 850 (1964).

[9] See, J. R. Morton, *Mol. Phys.*, **6**, 193 (1963).

irradiated $(KPO_3)_n$ condensed phosphate, no paramagnetic resonance could be observed at room temperature. This point is difficults to explain.

P_a and P_b Center.—The compositions of the phosphate glasses lie between one and three in the M/P ratio. Therefore, the quantity of alkali or alkaline-earth modifier in the phosphate glasses is much larger than that in silicate or borate glasses. As the proportion of the network-modifying atom is increased, the breakdown of the phosphorus-oxygen network occurs, and the average molecular weight of the phosphate anions is found to decrease quite rapidly with time toward a moderately low limiting value. The alkaline-metal or alkaline-earth metal occasionally associates with the chain anions by attaching oxygen atoms of the "End" groups.[5)]

The EPR intensity of P_a and P_b peaks increases in proportion to the alkaline or alkaline earth content under conditions of the same dosage. The line width, the position and the shape of resonance are dependent on the kind of alkaline or alkaline-earth incorporated. The formation of these centers becomes easier in the order $K<Na<Li<Ba\approx Ca$, and, according as the samples change from the vitreous state to the crystalline state, the formation of these centers seems to become more difficult. In the irradiated phosphate glasses of $Na/P=1$, these peaks disappear.

In the case of the alkaline-earth and alkaline-metal ions, it would be logical to expect that the tendency toward coordinate formation would increase with an increase in the charge/radius^2 ratio.[10)] The charge/radius^2 ratios for Ca^{2+}, Ba^{2+}, Li^{1+} and Na^{1+} are 3.4, 2.6, 1.7 and 1.0 respectively. Therefore, the stability of the coordinate formation may increase in the order $Na<Li<Ba<Ca$. As has been shown by Takahashi[11)] in studying the effect of network modifiers on the expansion coefficients of binary phosphate glasses, the expansion coefficient decreases in the order $K<Na<Li<Ba<Ca$, and decreases as the cation behaves as a network former rather than as a modifiers.

These facts suggest that, in phosphate glass modified with such ions as calcium, barium or lithium, which can coordinate with the tetrahedral oxygen atom in "End" groups, the weak resonance lines of two distinct types seem to appear easily; this is probably connected with the ability of coordinate formation.

In the region of the "End" group $(-PO_3)$, two, four or six nonbridging anions and some alkali cations as counter ions may be accidentally adjacent to each other, giving a localized region of excess negative charge. This configuration can trap holes.

The observed *g*-value of the P_a center which is larger than that of a free electron, as is shown in Fig. 2, suggests that the paramagnetic center is a trapped hole produced in the glass network by irradiation, as in the above discussion.

In the case of irradiated alkaline-earth phosphate glass, it appears that the P_a center consists of two different peaks which show a different fading speed to thermal annealing. However, the author believes that these two peaks may be the same type of center, while the electric coulombic field near these centers is different.

The *g*-value of the P_b center which is smaller than that of a free electron, as is shown in Fig. 2, suggests that the paramagnetic center is the trapped electron in the vicinity of alkaline or alkaline-earth ions. The difference between the *g*-value of the P_b center and the free electron value, $g=2.0023$, is contributed by the orbital magnetic moment. An electron in a paramagnetic ion is influenced not only by the applied magnetic field but also by the field due to its own orbital motion. It follows that the P_b center has an appreciable amount of orbital angular momentum: a 1s hydrogen atom-like model would give a poor approximation for the wave function of the center.

The change of the line width in proportion to the measuring frequency has not been observed. However, the author believes that the *g*-value and the width depend upon the electric coulombic field near the center and on its orientation in the diamagnetic field. The shape of the resonance in lithium phosphate glass exhibited a very high symmetry. The coordination number of the Li^+ ion is high in the glass. Therefore, the electric field around the lithium atom in the glass network would be of a considerably high symmetry. In contrast, the coordination number of the alkaline-earth ion is low. The electric field would be of a low symmetry. The shape of barium or calcium phosphate glass was observed to be of low symmetry.

In lithium phosphate glass containing a small quantity of an alkaline-earth modifier as an impurity, the position and the width of the resonance are different from that displayed in pure lithium phosphate glass, but the shape is substantially the same, as Figs. 2a and 2b

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10) A. E. Martell and M. Calvin, "Chemistry of the Metal Chalate Compounds," Prentics-Hall, Inc., New Jersey (1952).

11) K. Takahashi, "Binary Phosphate, Silicophosphate, Borophosphate and Aluminophosphate Glasses, their Properties and Structure," a report presented at the 6th International Congress on Glass, Washington, D. C., July, 1962.

show. If the resonances of the lithium center and the barium center are observed independently, these types of resonances would appear. Therefore, the electric field created by the oxygen atoms that are in the sphere around the lithium atom would be changed by the addition of an alkaline-earth impurity.

In short, the defect center in glass should be discussed from the viewpoint of the dynamic state of the glass structure and the stability of the glass structure.

Alumino Phosphate Glasses. — The network in aluminophosphate glasses is said to be formed by the interlinking of $(AlO_4)^{5-}$ and $(PO_4)^{3-}$ groups via bridging oxygens.5)

A paramagnetic center due to hyperfine interaction with the nucleus of a four-co-ordinated aluminum ion has been observed in irradiated alumino silicate glasses and a single crystal of qurtz contaminated with aluminum ions, and the aluminum center has exhibited a spectrum consisting of a six-line structure in the vicinity of $g=2.010$.1,2)

In the present investigation, thus, it was to be expected that a broad resonance caused by such a hyperfine interaction with a phosphorus and an aluminum nucleus would appear in the vicinity of $g=2.01$. However, samples of alumino alkaline phosphate glasses irradiated with γ-rays were not found to exhibit a six-line structure with a g-value of ca. 2.01. The formation of a paramagnetic center due to a four-co-ordinated aluminum atom in phosphate glasses would be protected against γ-ray irradiation.

In contrast, the EPR intensity of the outer side, ${}_{a}P_{a1}$ and ${}_{b}P_{a1}$, increases in proportion to the aluminum oxide content of the glass. The EPR spectra of these outer sides may arise from the defect centers due to the interstitial aluminum.

Summary

The EPR spectrum, consisting of a two-line structure and two other distinct types of weak resonances, obtained from irradiated phosphate glasses suggests that these paramagnetic centers are connected with the peculiar structure of phosphate glasses.

The two-line structure arises from an axially-symmetric hyperfine interaction of a hole with a ^{31}P nucleus. Two distinct types have been demonstrated: one is a trapped hole produced in the glass network, and the other is the trapped electron in the alkaline or alkaline-earth ion. In phosphate glasses modified with such ions as calcium, barium or lithium that can coordinate with the tetrahedral oxygen atom in "End" groups ($-PO_3$), the weak resonances seem to appear easily.

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