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The Electron Spin Resonance of Mn^{2+} Ion in Polyphosphate

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A part of cation in polyphosphate was replaced with Mn^{2+} ion. Zero-field splitting parameter D due to the crystal field with axial symmetry was estimated according to Allen's method from the ESR spectrum of Mn^{2+} ion. The value of D changes with the change in the state of polyphosphate, crystalline or glassy. As the degree of polymerization of sodium polyphosphate glass decreases, the value of D increases and approaches to the value corresponding to the crystalline state. These phenomena were interpreted as due to the disorderness of glassy state. The value of D was found to change with the variation of the kind of cation in polyphosphate. This was explained in terms of the effective cationic field.

Many solid substances can have two states, that is, glassy and crystalline. Polyphosphate also has these two states.[1] Many phosphates having different kinds of cations and various degrees of polymerization are included under the name of polyphosphate. The characters of solid polyphosphate, therefore, are affected by these factors.

The environment of one of lattice points, atom or ion, is regular in crystalline state, whereas it is irregular in glassy state. So it is expected that the crystal field in solid polyphosphate is affected not only by the kind of cation and the degree of polymerization, but also by the state, glassy or crystalline. On the studies of the crystal field, the phenomena of the zero-field splitting in ESR spectrum offer many valuable informations.[2]

Allen has recently advanced the method by which zero-field splitting parameter D can be estimated from the relative intensities of the hyperfine structure of the ESR spectrum of Mn^{2+} doped in methanol and 12 N HCl, each of which can take two states, glassy and crystalline.[3]

In the present paper, a part of the cation of polyphosphate was replaced with Mn^{2+} and its ESR spectrum was observed. The zero-field parameter D due to the crystal field with axial symmetry in polyphosphate was estimated with Allen's method.

Theoretical

As Mn^{2+} ion has $S=5/2$ and $I=5/2$, the hyperfine and fine structures are expected to occur in its spectrum. The spin Hamiltonian, therefore, is given by

$$\mathscr{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + A\mathbf{S}\cdot\mathbf{I} \tag{1}$$

The first term of the right side represents the Zeeman effect and the next term indicates the fine structure interaction induced by the crystal field with axial symmetry. The last term shows the hyperfine interaction between the electron spin and the ^{55}Mn nuclear spin. The ESR spectra for glassy and polycrystalline states consist predominantly of hyperfine structures of the allowed transitions from $|-1/2m\rangle$ to $|1/2m\rangle$ state and the forbidden transitions from $|-1/2m\rangle$ to $|1/2m+1\rangle$ or $|1/2m-1\rangle$ state, where $-1/2$ and $1/2$ denote the electronic spin magnetic quantum numbers and m is the nuclear spin magnetic quantum number.

For glassy and polycrystalline states, Allen[3] has derived the equation of the intensities of the allowed transitions by using the first-order perturbation theory.

$$\begin{aligned} I_m \propto 2 &- \frac{A^2(35-4m^2)}{2(g\beta H)^2} - \frac{5.334D^2}{(g\beta H)^2} \\ &- \frac{D^2(34.14)(35-4m^2)}{(g\beta H)^2} \\ &+ \frac{D^4(208)(35-4m^2)^2}{(g\beta H)^4} \end{aligned} \tag{2}$$

Using $A=95$ gauss and $H=3245$ gauss and extrapolating the relation between the relative intensity and the D value to larger D value, Allen's graph was obtained as shown in Fig. 1. This graph gives the relation between the ratios of the intensity of the hyperfine line of $m=-5/2$ to those of $m=-1/2$ and $-3/2$ and the zero-field splitting parameter D. These intensities were estimated from the signal height of the first derivative, although the line width must be included in the interpretations of the intensity. As the line width is broadest in $m=$

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1) M. Miura, A. Hasegawa and T. Fukui, This Bulletin, **39**, 1432 (1966).

2) B. Bleaney, H. R. S. and D. J. E. Ingram, *Proc. Roy. Soc.* (*London*), **A205**, 336 (1951).

3) B. T. Allen, *J. Chem. Phys.*, **43**, 3820 (1965).

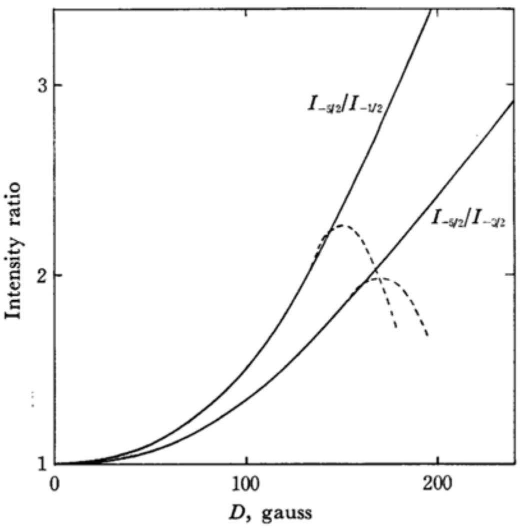

Fig. 1. Intensity ratios plotted against D.
The dashed line shows the curve from Eq. (2), the solid line the extrapolated curve from the calculated curve up to $D=120$ gauss.

$-5/2$ line, the estimated value of D must become larger, if the line width is taken into account. These widths of the hyperfine structures, however, showed no detectable change in any cases. Accordingly, no substantial problems as to the line width remain at the discussion in this paper.

Experimental

Manganese hydrogen phosphate dihydrate ($MnHPO_4 \cdot 2H_2O$), which was used as the source of Mn^{2+} ion, was purified by the recrystallization from its aqueous solution. The salt was added to the aqueous solution of sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), to give the molar ratio of the former to the latter of $10^{-4}:1$. The solution was evaporated to dryness. The product was heated at a temperature between 300 and 900°C in a furnace and then quenched with ice water.

Sodium polyphosphate melts at about 580°C. By the heat treatment at a temperature higher than 580°C, the glass of sodium polyphosphate was obtained, whereas by the treatment below its melting point, the crystal was gained. The crystal was also grown in the melt by slow cooling after heating at 900°C and seeding it.[1]

The samples used for studying the effects of crystallization water and polymerization on the D value were prepared by the following procedures. The crystal of $NaH_2PO_4 \cdot 2H_2O$ incorporated with Mn^{2+} ion was obtained by the recrystallization from the aqueous solution of their mixture. This crystal was evacuated and heated in a sample tube for ESR measurement. This treatment results in the elimination of water from the crystal following the polymerization of the orthophosphate. The amount of the water eliminated was determined gravimetrically. The progress of the polymerization was observed by paper chromatography.[4]

Polyphosphate glasses having various degrees of polymerization were prepared from $NaH_2PO_4 \cdot 2H_2O$ and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) by varing their mixing ratio. The degree of polymerization was determined by the pH titration method.

The glass and the crystal of polyphosphates with different cations were obtained by heating and then quenching the mixtures of phosphoric acid (H_3PO_4) and the following orthophosphates: dilithium hydrogen phosphate (Li_2HPO_4), magnesium hydrogen phosphate trihydrate ($MgHPO_4 \cdot 3H_2O$), calcium hydrogen phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) and barium hydrogen phosphate ($BaHPO_4$). Potassium polyphosphate was prepared from potassium hydrogen phosphate (KH_2PO_4).

ESR measurements of these polyphosphates were carried out at room temperature, except for the case particularly denoted, by using the spectrometer described elsewhere.[5]

Results and Discussion

The Effect of the Concentration of Mn^{2+} Ion. The effect of the concentration of Mn^{2+} ion on the ESR spectrum was examined for sodium polyphosphate glass. When the relative concentration of Mn^{2+} ion to phosphorus atom was lower than 10^{-3}, the line width observed was practically constant. Therefore, the relative concentration of 10^{-4} was selected for Mn^{2+} ion in the present work. One of the ESR spectra was shown in Fig. 2.

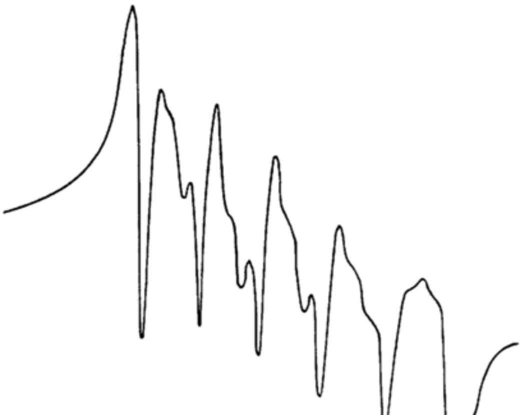

Fig. 2. ESR spectrum of Mn^{2+} in sodium polyphosphate glass.

The Effect of Heat Treatment Temperature on the Value of D. Sodium polyphosphate incorporated with Mn^{2+} ion was obtained by heating and quenching. The zero-field splitting parameter D of the Mn^{2+} ion estimated with Allen's graph is shown in Fig. 3 in relation to the heat treatment temperature. This figure shows that the parameter

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[4] H. Grunze and E. Thilo, *Sitzber. Deut. Akad. Wiss. Berlin, Kl. Math. Allgem. Naturw.*, **1953**, No. 5, p. 26 (1954).

[5] A. Hasegawa and M. Miura, This Bulletin, **40**, 2553 (1967).

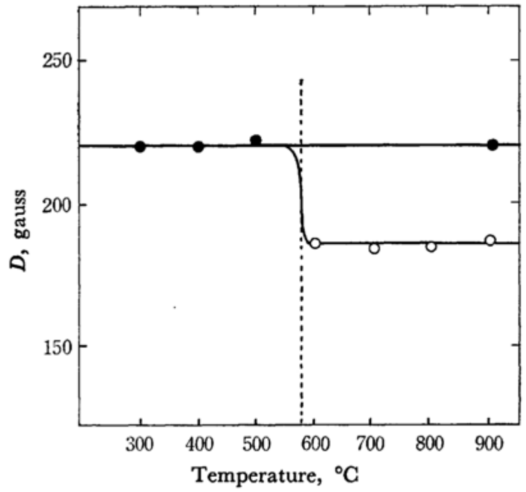

Fig. 3. The relation between D value and heat treatment temperature of sodium polyphosphate. ●: crystal; ○: glass. Dotted line shows the melting point.

D takes the value about 10% lower when treated above 580°C than that when heated below 580°C. This temperature is coincident with the melting point of sodium polyphosphate. By the treatment at a lower temperature than this, the crystal of sodium polyphosphate was obtained, whereas by that at higher temperature, the glass was obtained. The crystal of sodium polyphosphate was also obtained from the melt by cooling and seeding after heating at 900°C. The last crystal is known as Kurrol's sodium salt having very high degree of polymerization, *ca.* 10^4,[6] the D value of which is the same as that for the crystal obtained by heating at a temperature below the melting point. Thus, the D value depends largely on the state, crystalline or glassy, and has no relation to the degree of polymerization in case of the crystalline state.

The Effect of Water of Crystallization on the Value of *D*. The variation of the D value with the amount of the water of crystallization was investigated for $NaH_2PO_4 \cdot 2H_2O$ and the result obtained is given in Fig. 4.

The value of D increases first gradually, then abruptly with the progress of the elimination of water and finally takes a value which agrees with that for polyphosphate crystal. The water was removed by evacuating $NaH_2PO_4 \cdot 2H_2O$ in the initial stage at 50°C and finally at 260°C. Until almost all the crystallization water was eliminated, polymerization did not practically occurred, which was ascertained by a paper chromatographic method in both acidic and basic solvents.[4] The increase in the D value after the removal of all the crystallization water is due to the formation of pyrophosphate which was also ascertained by paper chromatography. The water of crystallization behaves to reduce the value of D. The water may coordinate to Mn^{2+} ion with high symmetry and shield the crystal field caused by phosphate anion from Mn^{2+} ion, resulting the decrease in the value of D.

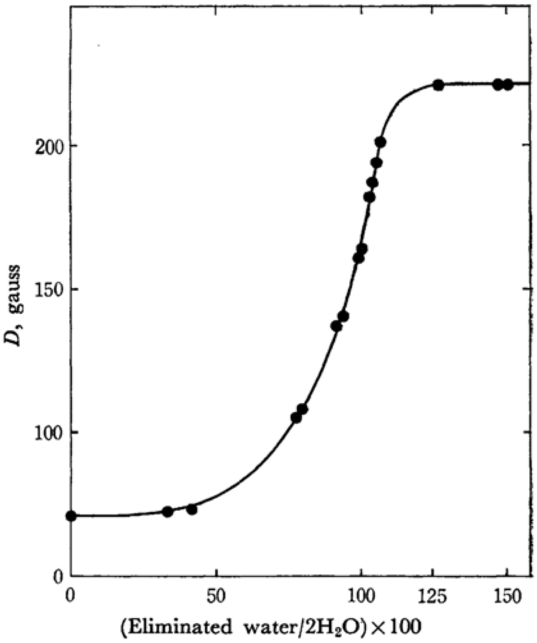

Fig. 4. The variation of D value with the elimination of water from $NaH_2PO_4 \cdot 2H_2O$. The positions of 50, 100, 125 and 150 on the abscissa mean the elimination of one of the crystallization waters and two of them and the formation of pyrophosphate and Kurrol's salt, respectively.

The difference between the D values for the glass and the crystal of sodium polyphosphate, which is seen in Fig. 3, is due to the amount of distortion on Mn^{2+} ion. When Mn^{2+} ion exists as an impurity in infinite regular lattice of crystal, certain amount of perturbation may be exerted to lattice by Mn^{2+} ion. The lattice thus perturbed produces the distortion on Mn^{2+} ion. In glassy state, however, such perturbation and distortion may be weakened by lack of the regular structure.

The interpretation described above, however, may encounter the following criticism. As the random structure in glassy state gives the D value having some distribution, the value obtained with Allen's method is an average one. Whereas, the D value in crystalline state is directly evaluated with the method because of the lack of the distribution. The variation in the D value due to the difference of the state may depend upon the distribution.

The Effect of the Degree of Polymerization. The glasses having different degrees of polymerization were prepared and their D values were estimated (Fig. 5). The value increases with the decrease in the degree of polymerization. The value extrapolated to triphosphate was coincident with the value

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[6] M. Miura and Y. Kubota, *ibid.*, **40**, 466 (1967).

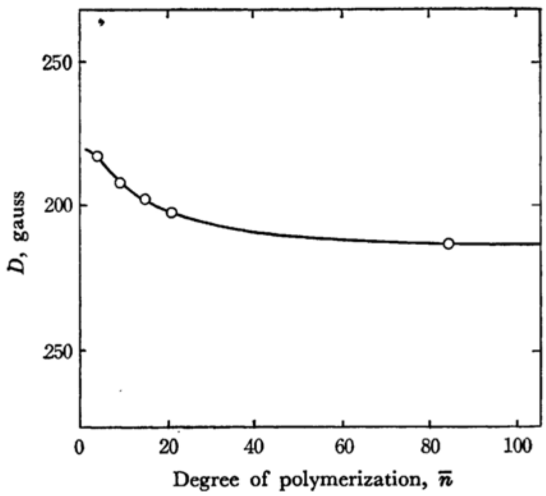

Fig. 5. The variation of D value with degree of polymerization of sodium polyphosphate glass.

obtained for the crystal of polyphosphate. This is closely correlated with the fact that the glass of triphosphate was not obtained by the method described here. The D value decreases accompanied with the increase in the degree of polymerization and approaches to the value for the glass in Fig. 3. This change, therefore, corresponds to the shift from crystalline state to glassy one, accompanied with the increase in the degree of polymerization of sodium polyphosphate glass. In the glass with low degree of polymerization, the environment of Mn^{2+} ion is considerably regular and is close to that in crystal.

The Effect of the Kind of Cation in Polyphosphate on the Value of *D*. The D values were also estimated for the glasses and crystals of polyphosphates having different kinds of cations. The D values for the crystalline states of polyphosphates with alkaline earth cations could not be estimated owing to their peculiar spectra. The difference between the cases of alkali and alkaline earth cations, therefore, can be insufficiently discussed with these data. Almost linear relations, as shown in Figs. 6 and 7, exist between the value of D and radius of cation[7]; the decrease in radius of cation causes the decrease in the D value.

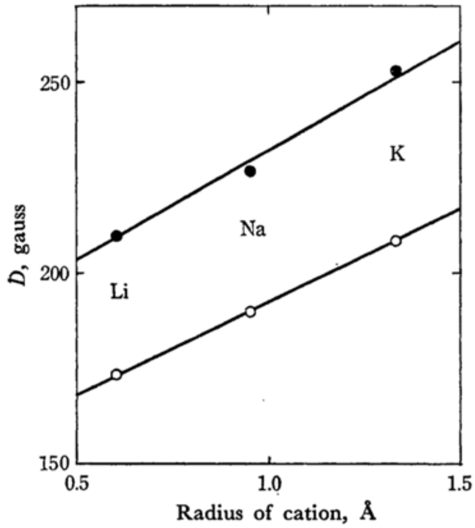

Fig. 6. The relation between D and radius of cation in alkali polyphosphate.
○: glass; ●: crystal

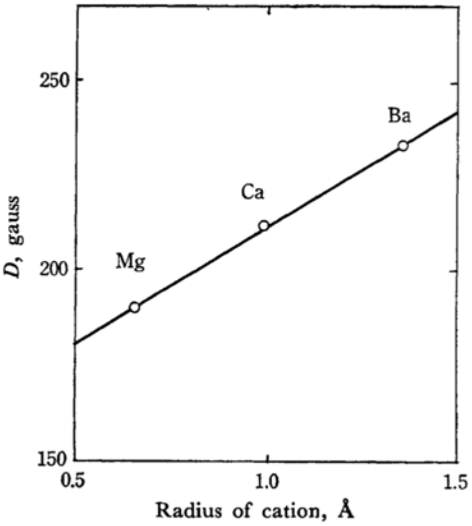

Fig. 7. The relation between D and radius of cation in alkaline-earth polyphosphate glass.

When cation with small radius strongly attracts the oxygen anions in polyphosphate by high effective cationic field, preferential coordination of the oxygen anion to Mn^{2+} ion is weakened. Thus, the center of the lone pair of oxygen may become more distant from Mn^{2+} ion and the value of D is considered to be reduced.

The Effect of Temperature on ESR Spectrum. ESR measurements of the glass and crystal of sodium polyphosphate were done at room temperature and the temperature of liquid nitrogen. ESR spectra obtained at both temperatures are essentially the same with each other. It may be concluded from this result that the value of D is not influenced by temperature and that the line width in the ESR spectrum of Mn^{2+} is not affected by relaxation mechanism.[8]

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7) L. Pauling, " Nature of Chemical Bond," 3rd Ed., Cornell University Press, Ithaca (1960).

8) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).