ESR Lineshape of Cu^{2+} and γ -Induced Cd^+ in Soda Borate Glasses

—Fluctuation of ESR Parameters and Structural Distribution in Glass—

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The fluctuation of ESR parameters which reflects the intrinsic “*site-to-site fluctuation*” in glass was extracted by analyzing the ESR lineshape of spin probes, Cu^{2+} and γ -induced Cd^+ , for the wide composition range of soda borate glasses. The results obtained are summarized as follows: (i) The lineshape of Cu^{2+} was closely reproduced by introducing a skewed distribution function of $g_{\parallel}$ into the lineshape function for polycrystalline matters. The skewed distribution of $g_{\parallel}$ is consequentially derived from the assumed gaussian distribution function of the ligand field strength.

The width of the $g_{\parallel}$ -distribution was found to vary with the composition of host glasses and increased in the order;

III < I < II, where I : $[\text{Na}_2\text{O}] (\text{mol}\%) \leq 13$, II : $20 \leq [\text{Na}_2\text{O}] \leq 37$, III : $55 \leq [\text{Na}_2\text{O}]$

(ii) The hyperfine lineshape of magnetic Cd^+ in the glasses was analyzed by assuming that the shape is completely controlled by the fluctuation of isotropic hyperfine coupling constant a . The fluctuation of a was estimated from the apparent line width and its order was found to be I $\cong$ III < II.

The variation of the fluctuation with Na_2O content and the difference between the magnitudes of fluctuations measured by Cu^{2+} and Cd^+ were discussed in terms of the bond strength of glass network and around the spin probes.

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ソーダ・ホウ酸塩ガラス中の Cu^{2+} と γ 線照射で生成した Cd^+ の ESR 線形 —ESR パラメーターのゆらぎとガラス中の構造分布—

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ソーダ・ホウ酸塩ガラスの広範な組成域でスピン・プローブである Cu^{2+} と γ 線照射で生成した Cd^+ の ESR スペクトルの線形を解析することによって、ガラスに固有な構造の分布を反映する ESR パラメーターのゆらぎを評価した。得られた結果は次のようにまとめられる。

(i) Cu^{2+} の線形は配位子場強度が構造のランダムネスを反映してガウス分布すると仮定し、それから変換で導かれるはずんだ形状をもつ $g_{\parallel}$ の分布関数を多結晶体に対する線形の表現に導入することにより、よく再現できた。 $g_{\parallel}$ のゆらぎの大きさはガラス組成に強く依存し、次の順に増大することが分った。

III < I < II,

ここで、I : $[\text{Na}_2\text{O}] \leq 13 \text{ mol}\%$, II : $20 \leq [\text{Na}_2\text{O}] \leq 35$, III : $55 \leq [\text{Na}_2\text{O}] \leq 70$ の組成域を表わす。

(ii) Cd^+ の超微細構造の線形は等方性超微細結合定数 a のゆらぎが線形を支配していると仮定して解析した。求められた a のゆらぎの大きさは I $\cong$ III < II の序列であった。

算出されたゆらぎの程度の Na_2O 含量とスピン・プローブの種類による差異を、ガラスのネットワークやプローブイオンのまわりの化学結合の強度に基づいて議論した。(1983年10月3日受付)

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1. Introduction

A glass is in a thermodynamic non-equilibrium state¹⁾. This fact originates from a random variation of local structures in glass, which will be hereafter referred to as “*site-to-site fluctuation*”. A given property of a glass, therefore, is viewed as the weighted average or sum of the responses from the distributed structures. Therefore, in the case of analyzing spectroscopic data on glassy matters, it is highly desirable to evaluate not only the mean values of the spectroscopic parameters but also their distribution, because the distribution contains the important information on glassy materials, the intrinsic “*site-to-site fluctuation*”.

In this paper we attempted to evaluate simultaneously the mean values and distribution of ESR parameters of Cu^{2+} or γ -induced Cd^{2+} ($\text{Cd}^{2+} + \text{electron} \rightarrow \text{Cd}^{2+}$) in soda borate glasses by analyzing the lineshape of ESR hyperfine structure (hfs) in detail. Both the paramagnetic ions had been proved to be useful and conventional spin probes for measuring the microscopic Lewis basicity of oxygen in oxide glasses²⁾⁻⁴⁾. Binary soda borate system was chosen because it has an extremely wide and continuous glass-forming region; the addition of small amount of alumina⁵⁾ eliminates the non-glass formation region with $38 \leq [\text{Na}_2\text{O}] \leq 66 (\text{mol}\%)$ ⁶⁾.

2. Theory

2.1.1 Analysis of ESR of Cu^{2+}

Stable isotopes of copper are ^{63}Cu (N. A. = 69.1%, $\mu = 2.22$, $I = 3/2$) and ^{65}Cu (30.9, 2.38, $3/2$). A Cu^{2+} has an electron hole on its d orbitals ($3d^9$). We can expect a quartet type hfs for an isolated Cu^{2+} .

We introduce here the first assumption :

(i) All the Cu^{2+} -complexes in these glasses take an elongated octahedral coordination belonging to D_{4h} symmetry (fig. 1)*.

According to the assumption (i), the follow-

Fig. 1. Assumed coordination of Cu^{2+} -complex in glass. The symbol H and θ indicate an applied magnetic field and orientation angle of the principal axis of the complex with respect to H .

ing spin-Hamiltonian with axial g and A tensors is used in the analysis ;

$$\mathcal{H} = g_{\parallel}\beta S_z H_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

where the symbols have their usual meaning. The resonance field can be given by the following equation as a function of an orientation-angle, θ , of the complex with respect to the applied magnetic field H ;

$$H(\theta, m) = (h\nu - mA)/g \cdot \beta \quad (2)$$

where

$$g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \quad (3)$$

and

$$A^2 = (g_{\parallel}^2 A_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 A_{\perp}^2 \sin^2 \theta)/g^2 \quad (4)$$

In deriving Eq. (2), the first order high field approximation was employed.

2.1.2 Characteristics of ESR lineshape of Cu^{2+} in glass³⁾

As had been pointed out in the previous papers^{3),7)}, no significant difference was seen between the perpendicular hf lineshapes for polycrystalline and glassy hosts ; the extra broadening, which originates from the “*site-to-site fluctuation*” in glass, was not observed for the perpendicular hfs. Thus, ESR parameters $g_{\perp}$ and $A_{\perp}$ can be regarded as scalars, not as statistically fluctuating variables, and only the lineshape of parallel hfs is fully analyzed, which has a marked host-dependence as shown in the following.

Figure 2 shows ESR hf structures (X- and K-band) of Cu^{2+} (with parallel orientation) in

* The other possible configuration proper to Cu^{2+} -complexes are incompatible with the observed line shape drawn in Fig. 5 (see 4.1), for they produce quite different g -values : $g_{\perp} > g_{\parallel} = 2.0$ holds for a compressed octahedral coordination. Such an example is seen in Cu^{2+} -crown ether complex in solution²³⁾. For tetrahedral coordination, the observed value is $g_{\parallel} = 0.74$ and $g_{\perp} = 1.531$ in ZnO (this spectrum is detectable only at the extremely low temperature such as 1.2 K)²⁴⁾.

Fig. 2. ESR spectra of Cu^{2+} in polycrystalline and glassy zinc metaphosphate (parallel hyperfine structures are shown). left : X-band spectra, right : K-band spectra

polycrystalline and glassy $\text{Zn}(\text{PO}_3)_2$. Three distinct differences were recognized between the lineshapes for both the hosts :

(1) In X-band spectra, the line width in "glassy spectrum" is fairly greater than that in "polycrystalline spectrum".

(2) The line width of "glassy spectrum" increases remarkably with increasing nuclear spin magnetic quantum number m (m -dependence). The peak with $m = +3/2$ is too broad to be discernible. Such a trend is not seen in "polycrystalline spectrum".

(3) In K-band "glassy spectrum", four hf components are united into a single envelope (ν -dependence). Unlike "glassy spectrum", the four peaks in "polycrystalline spectrum" are well resolved and have almost the same width as that in X-band.

The changes in temperature of measurement (77–300 K) and CuO concentration (0.01–2.0 mol%) bring no significant spectral change. These three features should be attributed not to the difference of spin-lattice or spin-spin relaxation times in both the hosts but to the existence of "site-to-site fluctuation" which is intrinsic to glass.

2.1.3 Simulation of "glassy spectrum"

Firstly, we consider the lineshape of Cu^{2+} in a polycrystalline host. This shape is called *powder pattern* $S_c(H)$, which corresponds to the total absorptions from the statistical ensemble of otherwise identical sites, each site randomly orientating with respect to the applied field, and described by Eq. 5⁸⁾ :

$$S_c(H) = \sum_m \int_0^\pi f[H - H'(\theta, m)] \sin\theta d\theta \quad (5)$$

Here, the symbol f expresses a convolution function, which reflects the line width and shape for a single crystal. Usually, the

lineshape function such as Gaussian or Lorentzian function is applied.

As will be shown later (4.1), $S_c(H)$ cannot reproduce the characteristic m - or ν -dependence of hf line width of "glassy spectrum" (see 2.1.2). Therefore, the distribution of spin-Hamiltonian parameters resulting from the intrinsic "site-to-site fluctuation" of the complex in glass must be introduced in order to simulate "glassy spectrum" closely.

Secondly, we discuss the method of introducing the intrinsic fluctuation into the analysis of the extraordinary lineshape of glass. Previous ESR studies^{2), 3), 7)} on Cu^{2+} in glasses revealed that only two ($g_{\parallel}$ and $A_{\parallel}$) of four parameters ($g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$) are sensitive to the change in chemical composition of host glasses. Here, we introduce the second assumption :

(ii) Only the ESR parameters that respond sensitively to the change in chemical composition of host glasses can be regarded reasonably as statistically fluctuating variables for a glass under consideration, others insensitive to the host composition being as scalars (constant values). On the basis of assumption (ii), it is sufficient to introduce a joint probability function $P(g_{\parallel}, A_{\parallel})$ having only two variables into the analysis, and the line shape, $S_g(H)$, for glassy matters is expressed by

$$S_g(H) = \sum_m \int_{A_{\parallel}} \int_{g_{\parallel}} \int_0^\pi P(g_{\parallel}, A_{\parallel}) f[H - H'(\theta, m)] \cdot \sin\theta d\theta dg_{\parallel} dA_{\parallel} \quad (6)$$

Equation (6) is not treatable as the basis of the simulation of "glassy spectrum", because it has two random variables. If possible, we have to derive the way of reducing the number of fluctuating variables in the joint probability function. The joint probability function $P(g_{\parallel}, A_{\parallel})$ can be degraded further to a probability function $P(g_{\parallel})$ by introducing the third assumption : (iii) the covalency, Γ_{σ} , of Cu^{2+} -O sigma-bonding on D_{4h} plane is independent of site in glass. This assumption was derived from the following observation : Figure 3 shows that Γ_{σ} can be regarded as constant (about 40%) over the extremely wide glass-forming region of $\text{Na}_2\text{O-B}_2\text{O}_3$ system. The covalency, Γ_{σ} , is defined by Eq. 7¹⁰⁾ :

$$\Gamma_{\sigma}(\%) = \frac{200(1-S)}{1-2S} (1-\alpha^2) \quad (7)$$

Fig. 3. Bonding parameters between cupric ion and ligand oxygen in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses³⁾.

where, S is an overlap integral between the related atomic orbitals.

Here, the coefficient α^2 is related to the spin-Hamiltonian parameters by the following equations^{2), 3), 21)};

$$\alpha^2 = -(A_{\parallel}/P) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04 \quad (8)$$

where P is a constant (0.036 cm^{-1}) concerning the radial part of the d orbital of Cu^{2+} . By combining Eqs. (7) and (8), the third assumption leads to the following relation:

$$g_{\parallel} - A_{\parallel}/P = \text{const.} \quad (9)$$

Equation (9) means that two variables, $g_{\parallel}$ and $A_{\parallel}$, are not simultaneously random but changes in concert with each other (this simple relation was firstly found by Imagawa²⁾). Therefore, two variables function $P(g_{\parallel}, A_{\parallel})$ can be reduced to one variable function $P(g_{\parallel})$ by employing Eq. (9). Then, Eq. (6) can be rewritten as Eq. (10);

$$S_g(H) = \sum_m \int_{g_{\parallel}/0}^{\pi} P(g_{\parallel}) f[H - H'(\theta, m)] \cdot \sin\theta d\theta dg_{\parallel} \quad (10)$$

Of course, this equation has the probability function with a single fluctuating variable.

The last problem is how to determine the shape of $P(g_{\parallel})$. We discuss this problem in terms of the ligand field theory. The origin of $g_{\parallel}$ -fluctuation of the distribution is ligand field strength E around Cu^{2+} , which is brought by the structural randomness in glass. Thus, the distribution function of E , $P(E)$, is related to $P(g_{\parallel})$ by the relation

$$P(g_{\parallel}) = P(E) / \left| \frac{\partial g_{\parallel}}{\partial E} \right| \quad (11)$$

Here, the denominator is the absolute value of the Jacobian associated with transformation from E to $g_{\parallel}$ given by Eq. (12)¹¹⁾;

$$g_{\parallel} = 2.0023 - 8\alpha^2\lambda_0/E \quad (12)$$

where, λ_0 is the spin-orbital coupling constant (-828 cm^{-1}) for free Cu^{2+} .

The distribution function $P(E)$ was assumed to be a simple Gaussian function on the basis of the fact that most of ligand field absorption spectra for glass can be deconvoluted by use of Gaussian component.

The simulation of ESR lineshape for glass can be, therefore, carried out by using Eqs. (10), (11) and (12). In the simulation, the width of $P(E)$ was modified so as to reach a reasonable fitting of the experimental spectrum by a trial and error method (the location of mean value of $P(E)$ is assumed to be equivalent to the apparent peak position of the ligand field absorption spectra³⁾). All the numerical treatments were executed on a computer.

2.2 Analysis of Cd^{2+} hyperfine structure in glass

2.1.1 Analysis of ESR hyperfine structure of Cd^{2+}

A Cd^{2+} doped into oxide glasses traps an electron and is converted into a paramagnetic Cd^{+} , when the glasses are subjected to an irradiation with an energetic photon. Stable isotopes of Cd are ^{110}Cd (N.A. = 12.75%, $\mu = -0.5922$, $I = 1/2$), ^{113}Cd (12.26, -0.6195 , $1/2$) and nuclei with zero nuclear spin (75%).

The Hamiltonian described by Eq. (13) is used in the analysis of Cd^{+} ESR;

$$\mathcal{H} = g\beta\mathbf{S} \cdot \mathbf{H} + a\mathbf{I} \cdot \mathbf{S} \quad (13)$$

which is characterized by isotropic g and A . For Cd^{+} nuclei with zero nuclear spin, of course, the second term is zero. For Cd^{+} with $I = 1/2$ the second term is greater than the first one in the Hamiltonian. The conventional high field approximation is not applicable and we have to use the Breit-Rabi solution^{11), 13), 16)}. Then, the resonance fields for a pair absorptions for magnetic Cd^{+} ($I = 1/2$) are given by

$$H_a = \frac{2h\nu}{g\beta} \frac{h\nu + a}{2h\nu + a} \quad (14)$$

and

$$H_b = \frac{2h\nu}{g\beta} \frac{h\nu - a}{a - 2h\nu} \quad (15)$$

Here, the suffix of H labels the possible transitions between eigen spin states.

2.2.2 Origin of extra-broadening in hf absorption of Cd^{+} in glass

As in the case of Cu^{2+} , the distribution of ESR parameters controls the ESR lineshape of Cd^{+} in glass. In the case of Cd^{+} , we introduce

the third assumption ; (iii) fluctuation of an isotropic hf coupling constant a controls practically the lineshape of Cd^+ hf absorption : The distribution of an anisotropic hf coupling constant and g values is assumed to affect negligibly the hf line shape of Cd^+ . The contribution of g -fluctuation to the line width has already found to be about one order smaller than that of $a^{(1), (12)}$. Therefore, the validity of this assumption can be confirmed by clarifying that the influence of anisotropic hf component on the line width is negligibly small. This was provided by the following observation. **Figure 4** shows hf lines of Cd^+ in polycrystalline and glassy $33 \text{CaO} \cdot 67 \text{B}_2\text{O}_3$. A distinct anisotropy of A-tensor was seen in the former, but its magnitude was found to be only 0.65 mT (1 Tesla = 10000 Gauss), it being estimated by employing our new solution⁽¹³⁾⁻⁽¹⁵⁾ to the spin Hamiltonian with axial g - and A-tensor and computer simulation technique. It is clear that the contribution of anisotropy in A-tensor to the line width for "glassy spectrum" is rather small.

Fig. 4. ESR hyperfine absorption of γ -induced Cd^+ in glassy (denoted by bold line) and devitrified (by dashed line) $\text{CaO} \cdot 2 \text{B}_2\text{O}_3$. Lineshape simulation of the latter was carried out in order to estimate an anisotropic component of hf-tensor, the result being shown in the upper right, where the solid is experimental spectrum and dotted line expresses the calculated trace.

2.2.3 Evaluation of fluctuation of a

As was pointed out in the previous paper⁽¹²⁾, the resonance field H_B is extremely sensitive to the slight change in a , the absorption being unobservable even in slightly disordered polycrystalline host. Thus, the component of an hf absorption corresponding transition A will be considered. Here, we develop a simplified

treatment discussing the relation the line width and the fluctuation in a instead of complete reproducing the experimental spectrum on a computer based on the distributed a -value. The standard deviation, σ_H , of the resonance field H is given by Eq. (16).

$$\sigma_H^2 = \left(\frac{\partial H}{\partial a} \right)_g^2 \sigma_a^2 + \left(\frac{\partial H}{\partial g} \right)_a^2 \sigma_g^2 + 2 \left(\frac{\partial H}{\partial a} \right)_g \cdot \left(\frac{\partial H}{\partial g} \right)_a \cdot \lambda_{g,a} \quad (16)$$

where we neglected the higher order differentials of a and g , and $\lambda_{g,a}$ means the covariance between random variables g and a . Recalling the third assumption and neglecting the second and third terms, we reach Eq. (17),

$$\sigma_H \doteq \left(\frac{\partial H}{\partial a} \right)_g \sigma_a = \frac{2h^2\nu^2}{g\beta(2h\nu + a)} \sigma_a \quad (17)$$

As non-linearity of the transformation between H_A and a (Eq. (14)) is rather small⁽¹²⁾, the following approximation is valid ;

$$\sigma_H = k \cdot \Delta H_{\text{msl}} \quad (18)$$

where ΔH_{msl} and k express the peak-to-peak width of the absorption in a derivative spectrum and a proportional constant, respectively. By combining Eqs. (17) and (18), the relation can be derived which connects the experimental line width, ΔH_{msl} , to the fluctuation, σ_s , of 5s-character (defined by a/a_{free}) of the magnetic electron on a Cd^+ ;

$$\sigma_s = \left[\frac{kg\beta(2h\nu + a)}{2h^2\nu^2 a_{\text{free}}} \right] \Delta H_{\text{msl}} \quad (19)$$

Here, a_{free} is the weighted average (0.4654 cm^{-1}) of a_{free} for ^{111}Cd and ^{113}Cd . By substituting the estimated g , a and ΔH_{msl} , one can derive the fluctuation of the 5s-character, which is the most fundamental parameter^{(9), (20)} in discussing the coordination geometry.

3. Experimental

3.1 Sample preparation

Sodium borate glasses of the batch composition $x\text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3$ (x : mol%) were prepared by conventional melt-quenching method. The compositions with $x=45$ and 55, which are in outside of usual glass-forming range⁽⁶⁾, were vitrified by adding 3 mol% of alumina⁽⁵⁾ or by employing twin-roller quenching technique. The samples obtained by above two methods gave the same results for the following measurements. There are two kinds, ^{63}Cu (I = 3/2, $\mu=2.22$, N.A. = 69%) and ^{65}Cu (3/2,

2.38, 31) of isotope for natural copper. In this experiment, CuO enriched to 99.9% ^{63}Cu (provided by Oak Ridge National Laboratory, USA) was used to remove the interference due to the absorption of the isotope. 0.5 mol% of CuO was added to each batch.

Glasses containing CdO were prepared by replacing 1 mol% of Na_2O with CdO. The detailed procedures of preparation were described elsewhere^{3), 12)}.

3.2 ESR measurements

The glasses doped with CdO were coarsely crushed and placed in fused silica glass tubes. Each tube was evacuated, sealed, and subjected to the γ -irradiation from a ^{60}Co source with the dose of 9.0×10^5 Rd at 77 K. X-band ESR spectra of the samples were obtained by use of a JEOL JES-PE-3 X spectrometer at 173 K without an intervening warm up to room temperature. The temperature was chosen so as to satisfy two conditions that no serious power saturation was observed at a few mW level of incident microwave and that no detectable structural relaxation of as-induced Cd^+ center was seen.

The ESR spectra of CuO-containing glasses were recorded at about 9 GHz (X-band) and 24 GHz (K-band). Most of the measurements were carried out at 25°C.

The applied magnetic field and the microwave frequency were calibrated by a proton NMR marker and a cavity wave meter, respectively.

4. Results and discussion

4.1 Cu^{2+} in soda borate glasses

Three different spectral patterns appeared, when alkali concentration is changed from 5 to 70 mol%**. These representative shapes were termed as spectrum I ($5 \leq [\text{Na}_2\text{O}] \leq 13$), II ($20 \leq [\text{Na}_2\text{O}] \leq 37$) and III ($55 \leq [\text{Na}_2\text{O}] \leq 70$), respectively³⁾. In the two boundary regions between the two adjacent composition regions, a superposition of the two patterns was observed³⁾. Spectrum I, II and III were reproduced by using the equations derived in 2.1 on a computer. Figure 5 exhibits the experimental line shapes (X-band) and the best fitted shapes, $S_g(H)$, which were obtained by introducing P

($g_{\parallel}$). The powder patterns, $S_c(H)$, were also shown in the figure, which were generated by using the same values of ESR parameters with the mean values of the distribution used in the calculation of the $S_g(H)$. It is obvious from the figure that $S_g(H)$ closely fits with the experimental shape for each pattern, whereas $S_c(H)$ cannot reproduce the characteristic m -dependence for "glassy spectrum". Furthermore, $P(g_{\parallel})$ employed in the simulation of X-band spectrum well reproduced the K-band spectrum as shown in Fig. 6. This fact means that the distribution $P(g_{\parallel})$ is highly reliable.

Figure 7 summarizes $P(g_{\parallel})$'s used in the simulation of the three representative shapes. Two features are recognized in respect of the shape and width of $P(g_{\parallel})$:

First, all the $P(g_{\parallel})$'s are not symmetric but skewed. Figure 8 illustrates graphically how symmetric Gaussian distribution in E , $P(E)$, (resulting from a statistical distribution of

Fig. 5. Three representative ESR line shapes of ^{63}Cu in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses ($\nu=9.439$ GHz).

a : Experimental trace, b : Generated powder pattern $S_c(H)$ (a Gaussian function with $\sigma_{\text{conv}}=1.0$ mT was employed as a convolution function), c : Simulated trace $S_g(H)$ involving the distribution function of $g_{\parallel}$. $P(g_{\parallel})$'s are shown in Fig. 7.

Fig. 6. Lineshape of spectrum II ($\nu=23.75$ GHz). a : Experimental trace, b : Generated powder pattern ($\sigma_{\text{conv}}=1.0$ mT), c : Simulated trace $S_g(H)$ using the same distribution function of $g_{\parallel}$ that employed for the X-band spectrum.

** Another spectral pattern, abbreviated as spectrum II', is seen in conventionally quenched glasses with Na_2O smaller than 5 mol%²²⁾. However, this shape cannot be regarded as the independent pattern, because it relaxed into spectrum I on annealing the glass.

Fig. 7. Distribution function of g -values used in the simulation of the experimental trace. I : Spectrum I, II : Spectrum II, III : Spectrum III. Note that distribution function of g_I is approximated by a delta-function.

Fig. 8. Schematic representation of the transformation from ligand field strength E to g_{II} . Note that symmetric distribution function of E ($P(E)$) is transformed to a skewed distribution of g_{II} ($P(g_{II})$).

ligand field strength in amorphous hosts) can give rise to a skewed distribution of g_{II} . Such a generation of a distorted distribution in a statistical quantity under consideration is consequent on the non-linear transformation of a symmetrical distribution of a quantity to that of another quantity. The degree of the distortion depends on both the strength of non-linearity in the transformation and on the width of the distribution. Thus, in contrast with spectroscopic data on polycrystalline matters a great care should be paid to the nature of the transformation between the quantities under consideration in extracting the significant informations from spectroscopic data on glassy matters. A typical example was seen in ESR of γ -induced Pb^{3+} in glass reported in Ref. 16).

The second characteristic is seen in the width of $P(g_{II})$. The evaluated width of $P(g_{II})$ differs from spectrum to spectrum, increasing in the order $III < I < II$. The distributing range of g_{II}

for II is overlapping fairly with those for I and III, whereas $P(g_{II})$ for I is separated completely from that for III. This result means that the ensemble of Cu^{2+} -complex giving spectrum I is entirely different from that for III and the ensemble of Cu^{2+} -complex yielding spectrum II contains Cu^{2+} -complexes responsible for I and III as a part of its elements.

4.2 Cd^{2+} in soda borate glasses

Figure 9 shows three ESR hf absorptions of magnetic Cd^{2+} in the glasses for which Cu^{2+} spectrum I, II and III were observed. The resonance field and line width varies conspicuously with varying soda content. The hf coupling constant a and ΔH_{msl} are plotted against Na_2O content in Fig. 10, a being evaluated from Eq. (14) (in which g -value was directly estimated from a singlet absorption appearing around 0.33 T due to a non-magnetic Cd^{2+}). With increasing Na_2O content the coupling constant a decreases monotonically with increasing Na_2O content, while the line

Fig. 9. Representative ESR line shape of Cd^{2+} hyperfine structure in $xNa_2O \cdot (99-x)B_2O_3$ glasses ($\nu = 9.2$ GHz).

a : $x = 9$, b : $x = 24$, c : $x = 69$. The symbol ΔH_{msl} expresses the peak-to-peak width.

Fig. 10. Effect of Na_2O upon the isotropic hyperfine coupling constant, a , of Cd^{2+} and the line width, ΔH_{msl} , of the hf absorption.

Fig. 11. Variation in the mean value and fluctuation of 5 s-character of the magnetic electron on a Cd^+ with the Na_2O content in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The fluctuation is normalized by the maximum value in the whole composition region examined. For comparison, the 5 s-character of Cd^+ in reference crystal was also indicated in the left of the figure. a : CaCO_3 (aragonite), CN (coordination number around Ca^{2+}) = 9, b : CaCO_3 (calcite), CN = 6, c : CaO , CN = 6.

width increases conspicuously near 15 mol% of Na_2O , reaches a maximum around 25 mol% of Na_2O and decreases gradually. By using Eq. (19), ΔH_{msl} is transformed to the fluctuation of 5 s-character of a magnetic electron on a Cd^+ . The magnitude of the s-character fluctuation, which is normalized by the maximum value obtained over the whole range in this system, is plotted in Fig. 11 along with the mean value of the 5 s-character. The estimated composition dependence of the fluctuation was found to be similar with that of $P(g_{\parallel})$ for Cu^{2+} ; the fluctuation is largest in the composition range of 20–25 mol% Na_2O and smaller in either of the adjacent regions. However, a significant difference may be noted between the response of Cd^+ and Cu^{2+} : The magnitudes of the distribution of 5 s-character for the lower soda and higher soda glasses are almost identical with each other, while the width of $P(g_{\parallel})$ in the latter (III) is fairly smaller than that in the former (I). This difference will be discussed in next section.

4.3 Relation between fluctuation of ESR parameters and chemical bonding of glass network or spin probe

It has been established hitherto that the magnitude of the fluctuation of ESR parameters for both Cu^{2+} and γ -induced Cd^+ conspicuously vary with Na_2O content of host glasses. This fact can be interpreted as follows: Alkali ions or any other structurally weak points in a glass and the incorporated Cu^{2+} or Cd^{2+} , the precursor

of Cd^+ , compete in taking their favorable geometry under the cooling process from the melt. The coordination shell with weaker bonds is considered to be more deformed than that with stronger linkages. As the strength of $\text{Cu}^{2+}-\text{O}$ or $\text{Cd}^{2+}-\text{O}$ bonding markedly increases on going from low to high alkali composition, the increase in the fluctuation may be attributed to the appearance in addition to the complex with a rather regular geometry. This well accounts for the fact that the magnitude of the fluctuation of $P(g_{\parallel})$ or a in medium alkali region II ($20 \leq [\text{Na}_2\text{O}] \leq 37$) is fairly greater than that in lower alkali one. It is of interest to compare the width of $P(g_{\parallel})$ for II ($20 \leq [\text{Na}_2\text{O}] \leq 37$) and III ($55 <$). The width for III is narrowest and is somewhat alike to that (i.e., null distribution) for polycrystalline matters. As Cu^{2+} forms stable complex with discrete borate anions such as ortho or pyroborate ion (the previous raman study revealed that these glasses are mainly comprised of ortho and pyroborate anions¹⁷⁾), such a narrow distribution is considered to result from the rigidity of the Cu^{2+} -borate complex. Furthermore, this explanation is confirmed by illustrating the following two extreme cases: First example is $[\text{Cu}(\text{OH})_4]^{2-}$ complex in DMSO (dimethyl sulfoxide)-water glass (1 : 1 in volume, its preparation method is described in Ref. 18)) and its spectrum is shown in Fig. 12. Note that even in glassy host, the line width is surprisingly so small that an isotope splitting due to ^{63}Cu and ^{65}Cu is observable as if for a regular polycrystalline matrix! In practice, its line shape can be precisely simulated as shown in Fig. 12 by a powder pattern $S_c(H)$ without introducing the distribution function $P(g_{\parallel})$. The bond strength of the glass network, which is framed up by hydrogen bondings, is very weak, whereas that

Fig. 12. ESR line shape of $[\text{Cu}(\text{OH})_4]^{2-}$ in DMSO-water glass (pH = 12.7) at -100°C . Note that the splitting due to the two isotopes of copper nuclei is seen in the peak $m = -3/2$. — : Experimental trace, : Generated powder pattern $S_c(H)$.

Fig. 13. Schematic representation of network structure in a) 75 PO·25 B₂O₃, and b) DMSO-water glasses.

Fig. 14. Schematic figure of the coordination geometry of Cu²⁺ (a) and Cd²⁺ (b) in borate glasses with higher Na₂O. Note that more rigid complex is formed in the left.

of Cu²⁺-OH⁻ bond is extremely strong because OH⁻ is highly basic³⁾.

Another extreme instance is Cu²⁺ in 75 PbO·25 B₂O₃ glass. Its spectral pattern is II not III³⁾, notwithstanding the B₂O₃ content is less than that in 70 Na₂O·30 B₂O₃ glass for which spectrum III was observed. This fact is considered to be ascribed to the bond strength and stereochemistry of Pb²⁺ in these glasses; Pb²⁺ forms covalent bondings with ligand oxygens, when basicity of the ligand oxygens is high. This gives rise to the pyramidal coordination of Pb²⁺, it being on the apex and its lone pair orbital pointing in a direction as illustrated in Fig. 13 (this coordination was clarified by analyzing the ESR spectrum of γ -induced Pb³⁺ in Ref. 9)). Most of orthoborate anions, which are expected from the average composition, cannot be regarded as free ions. In other words the orthoborate ions are linked to form a macro-anion by fairly strong B-O-Pb-O-B bondings. In this case, Cu²⁺-O and Pb²⁺-O bondings are in competition with each other in constructing each favorable coordination structure. Thus, spectrum II, not III, is supposed to appear.

The difference in the fluctuations in higher soda region measured by Cu²⁺ and Cd²⁺ is explained in a similar manner; that is, Cu²⁺ having available 3d orbital is possible to form more rigid complex with discrete borate anions than Cd²⁺ with closed shell electronic configuration (4d¹⁰). Therefore, the behavior of

Cd²⁺ in the higher soda glasses is similar to that of Cu²⁺ in 75 PbO·25 B₂O₃ glass. Such a situation is schematically illustrated in Fig. 14.

Finally, above statements are generalized as a figure that the structural distortion in glass, which produces the structural fluctuation, is shared by each structural unit in proportion to the difference in chemical bonding strength of intra/inter units, which are competing in taking their favorite geometry. It is of interest to note that such a figure is phenomenologically valid for the understanding of mechanism of the structural change in densified glass induced by applying high pressure¹⁹⁾.

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