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Electron Paramagnetic Resonance of Mn^{++} in vitreous and crystalline systems: $NaPO_3$ (Mn) and Na_2O-GeO_2(Mn)

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Chimica. — *Electron Paramagnetic Resonance of* Mn^{++} *in vitreous and crystalline systems*: $NaPO_3(Mn)$ *and* $Na_2O—GeO_2(Mn)$ (*). Nota di Carlo Bettinali (**), Paolo Granati (**) e G. Sementilli, presentata (***) dal Corrisp. G. Sartori.

RIASSUNTO. — È stato studiato l'assorbimento di risonanza paramagnetica del Mn^{++} nel $NaPO_3(Mn)$ e nel $Na_2O—GeO_2(Mn)$. Si sono studiati gli spettri in relazione alla concentrazione in Mn^{++} e allo stato vetroso e cristallino del materiale. Gli spettri sono stati eseguiti a temperatura ambiente e colla banda K. La derivata dello spettro di assorbimento di risonanza paramagnetica nel $NaPO_3$ con 0,1 % di Mn^{++} mostra sei linee principali e cinque coppie di linee secondarie. Devetrificando per riscaldamento il vetro $NaPO_3(MnO, 1\%)$ scompaiono prima le righe secondarie ed infine le righe principali. Si forma al loro posto un'unica banda con valore $g_{\text{eff.}}$ circa 2,00. Tale valore è all'incirca quello dello spettro presente nel vetro, ma mostrante splitting iperfine.

Aumentando la concentrazione del Mn^{++} a 0,5 % e al 5 % si ha un andamento analogo che nel caso della devetrificazione nel campione con 0,5 % di Mn scompaiono le righe secondarie e rimangono solo le linee principali. Nel campione col 5 % in Mn, invece, si ha una sola banda eguale a quella del campione a basso contenuto in Mn devetrificato.

Si sono discussi i possibili meccanismi che portano alla perdita di risoluzione: rilassazione, asimmetria, ed effetto di dipolo causato dalla interazione fra atomi di Mn. Assumendo, come sembra indicare il confronto fra i campioni a cristallinità crescente e quelli a concentrazione crescente, che i due processi siano identici si deve concludere che il processo di devetrificazione porta alla formazione di nuclei ricchi in Mn.

Ulteriori conferme possono essere fatte mediante spettri di ESR a bassa temperatura e nella banda X.

I germanati, anche a bassa concentrazione non mostrano risoluzione dello spettro e compaiono solo le sei righe principali. La devetrificazione porta alla scomparsa delle spettro di assorbimento a causa dell'allargamento della banda, con lo stesso meccanismo che dà luogo alla perdita dello splitting iperfine nel $NaPO_3(Mn)$.

INTRODUCTION.

The electron spin resonance (e.s.r.) absorption of paramagnetic ions in glassy and polycrystalline inorganic solids, having the same chemical composition, has been the subject of much study [1, 2, 3, 4]. The purpose of this type of research is to detect, experimentally, effects predicted from theoretical considerations. These include the effect of an asymmetric or a modified crystalline field, arising during the devetrification process; differences in the lattice relaxation effects; and dipole-dipole interaction between the paramag-

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netic atoms at increasing concentration. Another application of this type of research is to the study of crystallization mechanisms. In fact, paramegnetic ions which have been introduced into a glassy system to be devetrified can act as nucleating centers. Two mechanisms, for which the first steps are the following, may be operative: 1) precipitation of impurities after diffusion of dispersed atoms or groups and 2) the growth of crystals around structural units formed by impurities [5, 6]. The aim of the research in this laboratory is to investigate the behavior of some paramagnetic ions during devetrification in different glassy systems. Some results related to the Mn^{++} in germanate and metaphosphate glasses are given in this note.

EXPERIMENTAL.

The glasses have been prepared by melting reagent grade reactants in a Pt—Au crucible. The germanate glasses were prepared by melting pure germanium oxide and sodium oxide. Mn was introduced as $MnCO_3$ and the melting process was conducted in a slightly reducing atmosphere. The $NaPO_3$ glass was prepared by melting NaH_2PO_4 mixed with oxalic acid and $MnCO_3$ as previously described ( ). The e.s.r. spectra were measured at ambient temperature with a Hilger and Watts spectrometer, operated at 95 KMc resonating frequency. The samples studied were the following: 1 *a*) $NaPO_3$(0.1 mol % Mn) glass, 1 *b*) $NaPO_3$(0.5 mol % Mn) glass, 1 *c*) $NaPO_3$(5 mol % Mn) glass, 2 *a*) $Na_2O—GeO_2$(0.1 % Mn) glass, and 2 *b*) $Na_2O—GeO_2$(0.5 % Mn) glass.

RESULTS.

Fig. 1 shows the e.s.r. spectrum of the $NaPO_3$(0.1 % Mn) glass. Six main lines are present, and five couples of lines between the main lines appear. Fig. 2 shows two curves. Curve A is the e.s.r. spectrum of $NaPO_3$(0.5 % Mn)

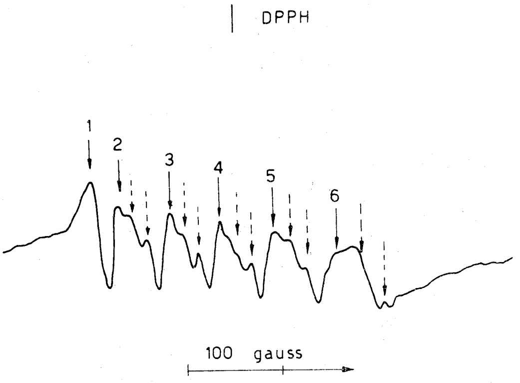

Fig. 1. – EPR derivative spectrum of $NaPO_3$ (0,1% mol Mn) glass.

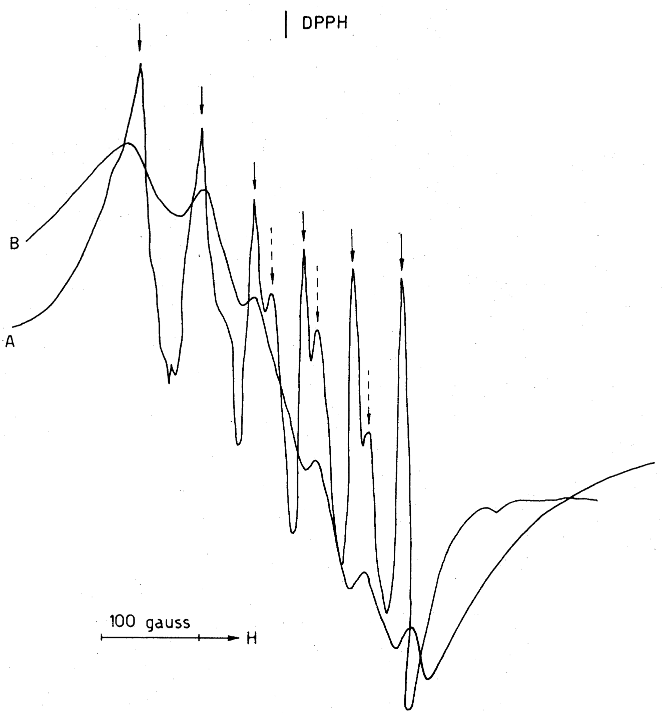

Fig. 2. – Curve A: EPR derivative spectrum of $NaPO_3$ (0,5 % mol Mn) glass; Curve B: EPR derivative spectrum of $NaPO_3$(0.5 % mol Mn) glass; heated 2 h at 260°.

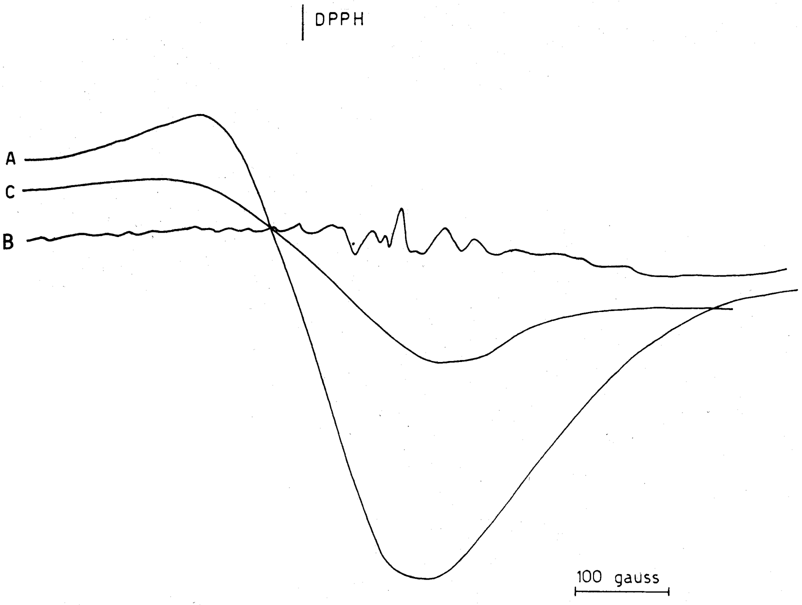

Fig. 3. – Curve A: EPR derivative spectrum of $NaPO_3$(0,5 % mol Mn) glass; Heated 24 h at 260°; Curve B: EPR derivative spectrum of $NaPO_3$(5 % mol Mn) glass; Curve C: EPR derivative spectrum of $NaPO_3$(5 % mol Mn) glass; heated 24 h at 260°.

glass having six main lines and some intermediate lines which are less evident and which seem to coalesce. Curve B is the spectrum of the previous sample heated four hours at 260°. This latter sample shows no crystallites under microscopic observation. The six main lines are again present but are less resolved and the intermediate lines are not seen. In contrast fig. 3, curve C shows the sample of fig. 2, curve A heated for forty-eight hours at 260° C.

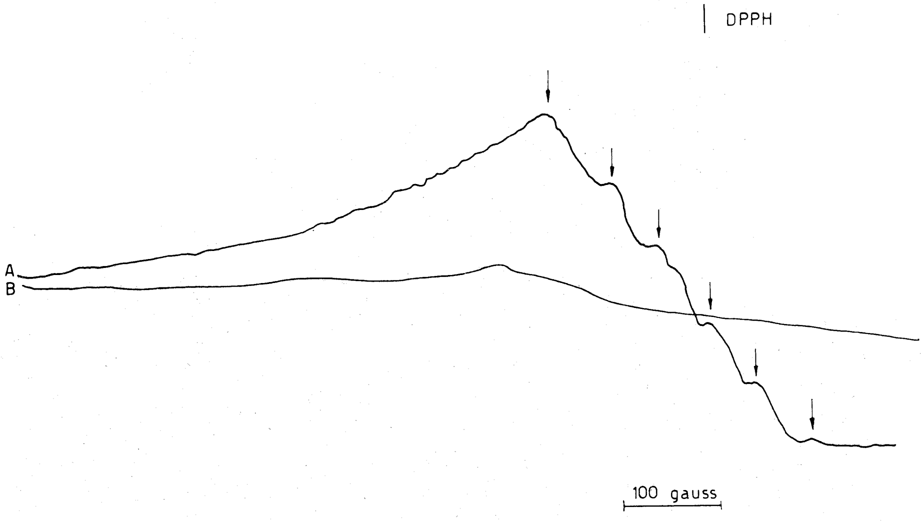

Fig. 4. – Curve A: EPR derivative spectrum of Na_2O—GeO_2(0,5 % mol Mn) glass; Curve B: EPR derivative spectrum of Na_2O—GeO_2(0,5 % mol Mn) glass; heated at 800° 2 h.

The sample is almost completely crystallized. No hyperfine splitting is present. In curve D, the $NaPO_3$(5 % Mn) glass, no hyperfine splitting is present under these conditions and the spectrum is very much like that of the devetrified sample containing 0.5 %Mn. In curve D the sample of curve heated at 260° for forty-eight hours is shown. Fig. 4, curve A shows the spectrum of the germanate glass containing 0.1 % Mn; the six main lines are present, but no intermediate lines can be seen. Curve B is the spectrum for the sample heated at 700° for xis hours. Under these conditions devetrification occurs and the e.s.r. signal practically disappears. This spectrum is similar to the spectrum of the germanate sample containing 0.5 % Mn.

DISCUSSION.

The observed spectrum of the $NaPo_3$(Mn) glass is very much like that of frozen $MnCl_2$ + LiCl solutions [3] at high LiCl concentration. At lower salt concentrations the Mn^{++} e.s.r. spectrum changes giving rise to a large band, as observed in the devetrified glass $NaPO_3$(MnO, 5.0 %), fig. 2, curve D. The loss of the hyperfine splitting can be related to at least three mechanisms, each one suggesting a different explanation of the role of the Mn^{++} ion during the devetrification process.

As is well known, the spin Hamiltonian of the Mn^{++} can be represented by [8]

$$A = gbHS + D' [S_z^2 - 1/3 (S (S + 1)] + A' SI \tag{1}$$

where g = spectroscopic splitting factor, b = the Bohr magneton, H = external spin operator and I = nuclear spin operator. The energy levels for the magnetic quantum numbers of electron spin M and nuclear spin m are expressed by the equation

$$E_{M_n} = gbHM + D [M^2 - 1/3 (S (S + 1)] + A' Mm + K' \{M [1 (I + 1) - m^2] -$$

$$- m [S (S + 1) - M^2]\} .$$

The last term is the result of a second-order perturbation calculation on the term A′ SI where K′ is given by $A'^2/2\,h\nu$. The resulting spectrum can give rise to six primary levels: M = 5/2, 3/2, 1/2, — 1/2, — 3/2, — 5/2 and 36 levels for $m = 5/2 \ldots$

The spectrum observed for glassy $NaPO_3$(0.5 % Mn) shows six main lines and five doublets. This type of spectrum can be explained starting from equation [1]. In the case of an axially symmetric fine structure term we observe only the $Mn = 1/2 \rightarrow M = - 1/2$ transitions. The five doublets can be attributed to forbidden $m = \pm$ transitions (m = nuclear magnetic quantum number) the main lines being the allowed $m = 0$ transitions. The presence of forbidden transitions has been explained [9] by a mixing of pure Mn states. If the mixing is small the mixed states are not very different from unmixed states and the approximate field positions for the forbidden transitions such as $1/2\, m + 1 \rightarrow - 1/2\, m$ are

$$H = H_0 - A (m + 1/2) + (A^2/2\, H_0)\, m\, (m + 1) + 1/4$$

and for $1/2\, m \rightarrow - 1/2\, m + 1$

$$H = H_0 - A (m + 1/2) + (A^2/2\, H_0)\, m\, (m + 1) - 67/4 .$$

For Mn^{++} I = 5/2 and therefore $H_0 = h\nu/gb$, and this produces five doublets.

A broadening of the e.s.r. spectrum of the $NaPO_3$(5 % Mn) and Na_2O—GeO_2(Mn) glasses has been observed. This can be related to many effects. *a*) Concentration effect. The dipolar interaction between two paramagnetic species is given by the classical relation $E_d = mr^{-3} (1 - 3 \cos^2 fi)$. For a sample with randomly oriented ions [4] the concentration contribution to the width of the line between points of maximum slope is given by the relationship

$$\Delta H = 2\, gb\, [3/5 (S (S + 1)]^{1/2}) \,(\text{summation}\ {}_{i \neq j} r_{ij}^{-6})^{1/2} .$$

The value of the average depends markedly on the distribution of ionic distances. For a completely random distribution it is approximately equal to 5 C where C is the volume concentration of paramagnetic ions. If the sample is not homogeneous the e.s.r. line width, due to this interaction, is a measure of a rather local concentration. In the case of devetrified samples the loss of hyperfine splitting can be related to the segregation of the Mn^{++} from the vitreous phase. *b*) Relaxation effect. The Stark effect of the electric field of the lattice gives rise to a transfer of the heat of magnetization between the magnetic spin system and the crystal lattice [10]. The thermal variation of the crystal lattice produces a periodic variation in the field acting on the ions and effects the energy of the orbitals. The interaction between spins and the lattice vibration is due to the spin-orbit coupling. To decrease the relaxation effect we must break the coupling, thus increasing the splitting of the crystal field, by means of ions such as Fe^{++}, or reduce crystal lattice vibration by decreasing the temperature. According to this effect the loss of the hyperfine splitting in our samples, when devetrified, can be related to a greater lattice vibration or to a reduced splitting of the levels in the crystalline phase. *c*) Anisotropy effects. If the crystal field is anisotropic, as happens in low symmetry crystals a greater mixing of the allowed M and forbidden *m* transitions can occur giving rise to the disappearance of the hyperfine structure [3]. Another explanation can be found if the second-order term for the fine structure for $M = 1/2 \rightarrow M = -1/2$ transitions is taken into account. A third possible effect related to anisotropy can be explained by examining the conventional spin Hamiltonian related to an ion in axial symmetry [11].

$$A = gb\mathrm{HS} + D\,[S_z^2 - 1/3\,S\,(S+1)] + F_a + AS_z\,I_z +$$
$$+\,B\,(S_x\,I_x + S_y\,I_y) - kb\mathrm{HI} + Q\,[I_z^2 - 1/3\,I\,(I+1)].$$

In the case of manganese $S = I = 5/2$. Since the direction of the magnetic field is the same as that of the quantization axis, the allowed transitions pertaining to the electronic part of the spectrum are given to second order for the $M = 1/2 \rightarrow M = -1/2$ transitions by the expression

$$H = H^0 + (16\,D^2/H^0)\cos^2 \sin^2\theta - (2\,D^2/H^0)\sin^4\theta .$$

The effect of this term is to widen the related lines until the spectrum is no longer observable.

The broadening of the e.s.r. spectrum observed in glassy samples at high Mn concentration and in the devetrified samples having a lower Mn content, can both be related reasonably to the same effect, that is to say a concentration effect. It is also possible that a different type of effect such as a relaxation or anisotropy can give rise to e.s.r. spectral broadening in the crystalline samples. A relaxation effect would imply that in the crystalline phase the lattice vibrations are larger than in the glass phase. However, since the energy content of a glass phase is higher, this explanation is not very probable. It is more likely that a large splitting of levels can occur in the crystalline phase. The anisotropy effect implies a greater influence of the crystalline field in crystals than in glasses: this is a very likely hypothesis. The discrimination between these possibilities can be reached through a more detailed analysis of the e.s.r. spectra at low temperatures, or by a greater understanding of the Mn^{++} influence in the devetrification process of the glasses studied.

CONCLUSIONS.

The e.s.r. absorption of Mn^{++} in $NaPO_3(Mn)$ and $Na_2O—GeO_2(Mn)$ systems is influence by both Mn concentration and crystallinity of the samples studied. It is therefore possible, by evaluating the e.s.r. absorption of these systems to obtain a better insight into the position of the Mn^{++} ion in glasses and the importance of minor paramagnetic elements in the devetrification process.

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