

ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} IONS IN KCl AND KBr

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It is shown that the hyperfine structure of electron paramagnetic resonance (EPR) spectra of Mn^{2+} ions in KCl and KBr crystals grown from aqueous solutions of these salts are probably due to "microvolumes" of aqueous solution enclosed in the regions of macroscopic defects. Comparative measurements of the hyperfine splitting made for aqueous solutions and crystal samples have shown that the structure of paramagnetic centres is identical. On the other hand additional observations made on KCl: Mn^{2+} samples crystallized from fused salt and from aqueous solution have proved that the structure of paramagnetic centres is different for these two kinds of samples. These results contradict that so far commonly accepted hypothesis according to which Mn^{2+} ions enter the crystal lattice of alkali metal halides crystallized from aqueous solution.

1. Introduction

It was shown in the papers devoted to the study of EPR of Mn^{2+} ions in alkali metal halides [1, 2] that the resonance spectrum is strongly influenced by thermal treatment and growth conditions of the crystals. Some unclear points in the results obtained with alkali metal halides grown from aqueous solution [1, 3] stimulated the authors of the present paper to investigate this problem more carefully.

The spectra of KCl: Mn^{2+} , KBr: Mn^{2+} , KJ: Mn^{2+} grown from aqueous solution are at room temperature identical, and consist of six hyperfine structure lines. When the temperature of the sample is decreased to the temperature of liquid nitrogen this spectrum disappears. It appears again (with the hyperfine structure of six lines) after heating the crystal to room temperature. If, however, the sample is annealed at a temperature higher than about 400°K then after cooling to room temperature the EPR spectrum has only one stable line with the half-width equal to 45 ± 1 Gs.

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There have been several papers dealing with the EPR spectra of crystals of potassium halides containing Mn^{2+} crystallized from fused salt [2, 5, 6, 7, 8]. Some attempts of interpreting the observed spectra and identifying the structure of paramagnetic centres can be found in Refs [1, 2, 6].

It can be shown, however, that the $\text{KCl}:\text{Mn}^{2+}$ crystal grown from fused salt by slow cooling has only one narrow line of Lorentz shape with the half-width of about 220 Gs in the EPR spectrum. The width of this line reduces after repeated slow annealing to 45 ± 1 Gs and only long thermal treatment of the sample gives rise to the appearance of fine and hyperfine structure in the EPR spectrum.

The purpose of the present report is to draw attention to the possibility of "counterfeiting" the results of observations by "microvolumes" of aqueous solution built-in into the crystal lattice of the investigated crystal. In our opinion, during the crystallization process some "microvolumes" of aqueous solution from which the crystal is grown are enclosed in macroscopic defects in the crystal. Thus the factor which is responsible for the hyperfine structure of the spectrum, at least in the case of crystals grown in aqueous solution, is according to our opinion just the solution confined in microdomains of the defected crystal.¹

2. Results of measurements

To check the validity of the above-mentioned hypothesis measurements of EPR spectra have been made for KCl and KBr crystals grown from aqueous solution and doped with bivalent manganese by adding suitable amount of MnCl_2 . The crystals were obtained from aqueous solution by slow evaporation. A part of the crystals grown by means of this method did not reveal any paramagnetic absorption. The samples which did not show paramagnetic absorption were characterized by very small dielectric losses compared to the dielectric losses of samples showing resonance spectra with hyperfine structure.

The measurements of the EPR spectra were made by means of a r. f. spectrometer ($\lambda = 3.2$ cm) with a transmission cavity and modulating frequency $f_M = 975$ kHz. The standard for calibration of the field was $\text{MgO} + 0.002\% \text{Mn}^{2+}$ [9].

The majority of information and evidence in favour of the hypothesis that the resonance spectrum of potassium halides containing manganese comes from "microvolumes" of aqueous solution, is provided by the comparison of the total splitting and the hyperfine structure constant A for crystals and aqueous solutions from which these crystals were grown. The spectra of Mn^{2+} in the crystal and in aqueous solution with the concentration of 1% mol. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ are shown in Figs 1a and 1b.

The positions of the resonance peaks in both spectra are given by the formula:

$$H^* = H_0 - Am - \frac{A^2}{2H_0} [I(I+1) - m^2] - \frac{A^2}{2H_0} m(2M-1)$$

¹ A detailed study of this problem has been made by one of the authors (J. Wiechula, *Ph. D. Thesis* to be submitted to the Faculty of Mathematics, Physics and Chemistry of the Wrocław University).

for the transitions $M, m \rightleftharpoons (M-1), m$: where m and M are the quantum numbers of the nucleus and electrons, respectively, and $H_0 = \frac{h\nu}{g\beta}$ [10]. The value of the total splitting of the Mn^{2+} spectrum is the same for KCl and KBr crystals and for the solution from which these crystals were grown. The agreement is better than 1%.

The hyperfine structure constant A is a quantity which depends on the surrounding environment of the paramagnetic ion [11]. In the case of the investigated crystals and solutions it is the same and amounts to 95 ± 1 Gs. In aqueous solution the Mn^{2+} ion is surrounded by water molecules. The equality of the quantity A in crystals and in solution favours our hypothesis that in KCl and KBr crystals grown from aqueous solution the Mn^{2+} ions are also surrounded by water molecules.

Aqueous solution of MnCl_2 is characterized by an isotropic spectrum without fine structure [12, 13, 14]. The lack of fine structure in the Mn^{2+} spectrum in aqueous solution is the result of the fact that the fine structure of the spectrum does not contain any isotropic lines. As a result of random distribution of local electric fields with respect to the external magnetic field there occurs considerable line broadening which does not permit a registration of the spectrum [15].

If, however, the central line of the fine structure is almost isotropic then the line is sufficiently narrow to be registered. Since the spin of the ^{55}Mn nucleus is $I = 5/2$ we observe instead of one line — six hyperfine structure lines (see Fig. 1a).

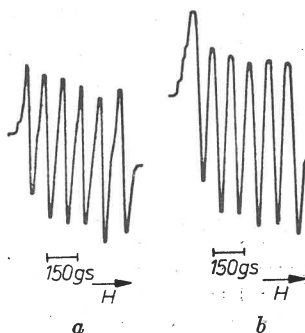


Fig. 1. Paramagnetic-absorption spectrum of: a) aqueous solution of KBr+1% mol. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, b) a crystal grown from this solution

When the KCl and KBr crystals which contain Mn^{2+} ions and were grown from the solution, are annealed for several hours at 400°K , the hyperfine structure disappears and only one line of Lorentz shape and with the half-width of about 45 Gs is observed (Fig. 2). During the heating of the crystal the "microvolumes" containing the solution evaporate and the manganese impurities are accumulated in the vicinity of grain boundaries forming aggregations. As a result of strong exchange interactions the line becomes narrower. The line is now similar to the EPR line of KCl : Mn^{2+} crystals obtained from fused salt by slowly cooling.

Fine grinding of the KBr : Mn^{2+} and KCl : Mn^{2+} crystals grown from aqueous solution gives also rise to the evaporation of water contained in the crystal and a decay of the hyperfine

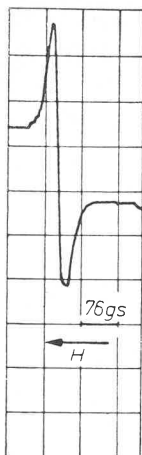


Fig. 2. EPR spectrum of $\text{KCl}:\text{Mn}^{2+}$ crystal grown from aqueous solution and heated to 400°K

structure. Manganese ions which in this case are not aggregated should give a broad spectrum which is difficult to be observed. The grinding of $\text{KCl}:\text{Mn}^{2+}$ crystals grown from fused salt and subjected to thermal treatment [2, 6] gives only rise to a decay of the anisotropic part of the spectrum (Fig. 3b). In this situation there remains the spectrum which corresponds to the transitions $M = 1/2 \rightleftharpoons -1/2$.

The measurements of the spectrum made at the temperature of liquid nitrogen gave a negative result. Paramagnetic absorption lines were observed neither in the case of crystals nor solution. The EPR spectrum of $\text{KCl}:\text{Mn}^{2+}$ crystals grown from fused salt does not show any change when the temperature is decreased from 300°K to 77°K .

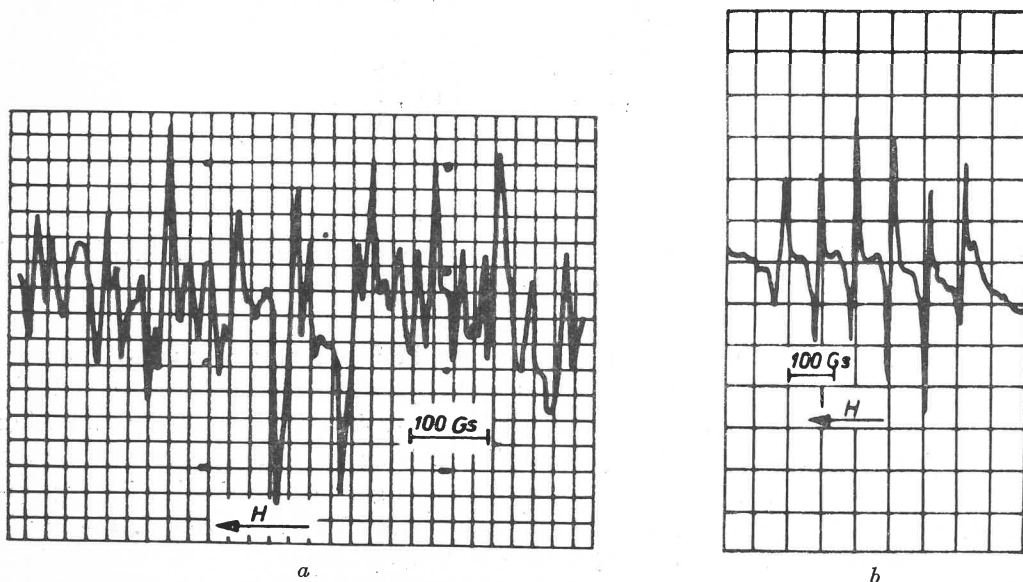


Fig. 3. EPR spectrum of: a) $\text{KCl}+0.1\%$ mol. MnCl_2 crystal grown from fused salt after annealing (center part of the spectrum), b) after grinding at room temperature

For the sake of comparison similar measurements have been made on KClO_3 and NaClO_3 crystals grown from aqueous solutions containing Mn^{2+} ions. The spectra obtained were identical as in the case of $\text{KCl}:\text{Mn}^{2+}$ and $\text{KBr}:\text{Mn}^{2+}$. These results also indicate a build-up of "microvolumes" of the solution into the crystal. The paramagnetic absorption in slowly crystallizing KClO_3 was much greater than in the case of very well growing NaClO_3 crystals. Fig. 4 shows the spectrum obtained from a $\text{KClO}_3:\text{Mn}^{2+}$ crystal grown from aqueous solution.

The microvolume hypothesis is also confirmed by measurements made by Breivogel and Sarkissian [17] who have studied the compounds K_2ZnCl_4 , K_2ZnBr_4 , K_2ZnJ_4 , K_2HgCl_4 ,

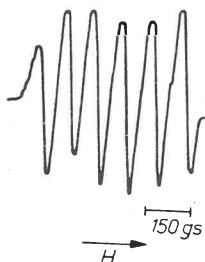


Fig. 4. EPR spectrum of $\text{KClO}_3 + 10\%$ mol. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ grown from aqueous solution

and CsZnCl_4 containing 0.1% mol. Mn^{2+} , grown from aqueous solution. These authors obtained almost the same value of the hyperfine structure splitting constant, equal to about $A = -89 \times 10^{-4} \text{ cm}^{-1}$ (about 95 Gs) which is characteristic for aqueous solution of MnCl_2 for such concentration.

3. Conclusions

It follows from all the discussed measurements and observations that it is highly probable that the "microvolumes" of the solution from which the crystals are grown and which are confined in macroscopic defect regions are responsible for the observed hyperfine structure of the EPR spectrum.

No observed fact contradicts this hypothesis. Moreover

1) the attribution of hyperfine structure to the Mn^{2+} ion in potassium halides would imply that the paramagnetic impurity ions occupy cation vacancies in such crystals. This is, however, rather improbable because of the difference in the radii of the respective ions, $\text{K}^+ = 1.33 \text{ \AA}$ and $\text{Mn}^{2+} = 0.80 \text{ \AA}$, which is too big [6].

2) Watkins and Yoshimura have shown that manganese is built up into KCl in the form of colloidal K_2MnCl_6 and only after very long thermal treatment a very small fraction of Mn^{2+} ions occupy cation vacancies in the crystal (solution energy of MnCl_2 in $\text{KCl} = -2.08 \text{ eV}$, and in $\text{NaCl} = +0.45 \text{ eV}$) [6], giving rise to hyperfine structure of the spectrum.

3) It turned out (Fig. 2) that annealing (thermal treatment) of samples grown from the solution leads to destruction of the hyperfine structure of EPR.

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