EPR Study of Mn^{2+} in $Hg(ClO_4)_2 \cdot 6\,H_2O$ Single Crystals *

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Z. Naturforsch. **35a**, 1304–1307 (1980); received July 9, 1979

The electron paramagnetic resonance of Mn^{2+} in $Hg(ClO_4)_2 \cdot 6H_2O$ has been studied at X-band at 298 K and 77 K. Mn^{2+} is found to substitute Hg^{2+}. The spectra have been analysed using the spin-Hamiltonian appropriate for trigonal symmetry. From the unequal separations between the $\Delta m = \pm 1$ doublets in $M = +1/2 \to -1/2$ transitions, the value of the axial part of the quadrupole coupling constant is determined. The observed doublet separations of forbidden hyperfine transitions in $M = +1/2 \to -1/2$ are in good agreement with those calculated.

1. Introduction

Electron paramagnetic resonance (EPR) of Mn^{2+} has been studied in a variety of lattices. However, EPR of Mn^{2+} in mercury salts has been restricted to $A_{II}B_{IV}$ compounds [1]. The possibility of introducing ions of transition elements into crystals of other mercury compounds has not been investigated previously. This paper reports the EPR of Mn^{2+} in hexaquomercury (II) perchlorate, $Hg(ClO_4)_2 \cdot 6H_2O$, single crystals at 298 K and 77 K.

2. Crystal Structure and Experimental Details

$Hg(ClO_4)_2 \cdot 6H_2O$ is isostructural with $Cd(ClO_4)_2 \cdot 6H_2O$ and crystallizes in trigonal symmetry with space group $P\bar{3}m1$ (D_{3d}^3) [2]. The unit cell, having the dimensions: $a = 8.005$ Å, $c = 5.344$ Å, contains one formula unit. The Hg atom and the two Cl atoms occupy special positions on the three-fold axis (D_{3d} and C_{3v} [2]). The Hg^{2+} is surrounded by an octahedron of water molecules elongated along the three-fold axis. The six Hg-O bonds are equivalent with a bond length of 2.341 Å [2]. The $[Hg(H_2O)_6]^{2+}$ complexes are held together by weak hydrogen bonds. The tetrahedral ClO_4^- group is slightly elongated along the c-axis.

Hexaquomercury (II) perchlorate was prepared by the method described by Johansson and Sandstrom [2]. $Hg(ClO_4)_2 \cdot 6H_2O$ single crystals containing 0.3% by weight of $Mn(ClO_4)_2 \cdot 6H_2O$ were grown by the method described earlier [2, 3]. The details of experimental set up for recording the EPR spectra are given in [3].

3. Results and Discussion

3.1 *Allowed Transitions*

For an arbitrary orientation, the EPR spectrum consists of a number of lines corresponding to allowed ($\Delta M = \pm 1$, $\Delta m = 0$) and forbidden transitions ($\Delta M = \pm 1$, $\Delta m \neq 0$). Angular variation study of Mn^{2+} spectra reveals the presence of only one manganese centre indicating that Mn^{2+} occupies identical sites in the lattice. Figure 1 shows the EPR spectrum of Mn^{2+} for magnetic field parallel to the z-axis at 298 K. The transitions in this spectrum are the allowed ones. The linewidth shows a weak angular dependence, and it is ≈ 2.0 mT along the z-axis.

Figure 2 shows the angular dependence of the allowed fine structure transitions ($\Delta M = \pm 1$) (θ variable). It is seen from the angular variation

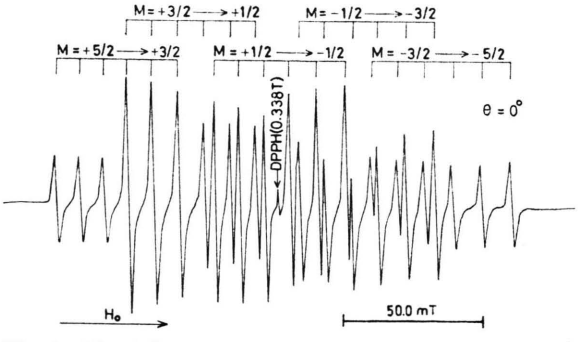

Fig. 1. The EPR spectrum of $Hg(ClO_4)_2 \cdot 6H_2O{:}Mn^{2+}$ single crystals at 298 K; with $H_0 \parallel z$-axis.

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* Revised Version was received October 16, 1980.

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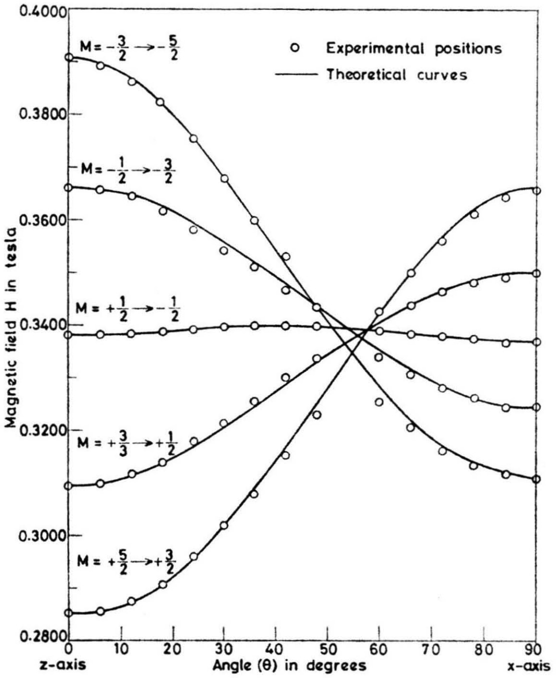

Fig. 2. Angular variation of the allowed fine structure transitions in the EPR spectrum of $Hg(ClO_4)_2 \cdot 6H_2O{:}Mn^{2+}$ at 298 K.

plot that the fine structure transition lines gather rapidly as θ changes from the z-axis ($\theta = 0°$). The lines collapse to a very small spread at an orientation $\theta = \sim 54.5°$ away from the z-axis. As θ increases further, the lines cross each other and spread out to a second maximum at $\theta = 90°$. The angular variation of the spectrum in a plane perpendicular to the z-axis shows no change in the positions of fine structure transitions, and any variation is usually within the experimental error. This indicates that the crystal field symmetry at the Mn^{2+} site is axial. The conservation of symmetry about the three-fold axis indicates that Mn^{2+} substitutes Hg^{2+} in the lattice to form $[Mn(H_2O)_6]^{2+}$ complex. The presence of only one manganese centre is consistent with the chemical formula.

The EPR spectra observed at 298 and 77 K have been analysed using a spin-Hamiltonian appropriate for Mn^{2+} in a trigonal crystalline field [4, 5]. The parameters of Mn^{2+} in $Hg(ClO_4)_2 \cdot 6H_2O$ are listed in Table 1. The signs of the parameter are only relative and have been determined from the observed second-order hyperfine shift, assuming $A_{\|}$ to be negative. Table 1 also includes the parameters of $Cd(ClO_4)_2 \cdot 6H_2O : Mn^{2+}$ [5] for comparison.

From Table 1 it is seen that the g-factor, which is independent of temperature, deviates slightly from the free spin value and shows a small anisotropy. The fact that the crystal field parameters have non-zero values and that the g-factor deviates slightly from the free spin value shows that the ground state is not exactly $^6S_{5/2}$. The value of the hyperfine splitting constant is isotropic and independent of temperature within the experimental error. It is of the same order as observed in other crystals where Mn^{2+} is sourrounded by six water molecules [6]. This indicates that Mn^{2+} in $Hg(ClO_4)_2 \cdot 6H_2O$ is surrounded by six water molecules. From Table 1, it can be seen that the value of the parameters b_2^0 and $[(2b_4^0)_c - 3b_4^0]$ are insensitive to temperature. It is also noticed from the Table that the value of b_2^0 is large for $Hg(ClO_4)_2 \cdot 6H_2O$ than for $Cd(ClO_4)_2 \cdot 6H_2O$. However, the values of the other parameters are virtually the same in both salts. The differing values of b_2^0 of Mn^{2+} in these two salts indicate that they differ greately in the static crystal field seen by the Mn^{2+} at divalent sites. The crystal field strength is in general determined by two factors: the electric field from the surrounding ions and covalency effects. In the present case, the difference in covalency is negligible, as is obvious in the hyperfine constant. The crystal field is, therefore, presumed to be mainly due to an octahedron of water molecules oriented

Spin-Hamiltonian parameters	$Hg(ClO_4)_2 \cdot 6H_2O$		$Cd(ClO_4)_2 \cdot 6H_2O$ [5]
	298 K	77 K	298 K
$g_{\|}$	2.003 ± 0.002	2.004 ± 0.002	2.0012 ± 0.001
$g_{\perp}$	2.009 ± 0.003	2.003 ± 0.003	1.9999 ± 0.001
b_2^0	138.96 ± 1.0	142.58 ± 1.0	44.65 ± 1.0
$[2(b_4^0)_c - 3b_4^0]$	8.69 ± 1.0	8.42 ± 1.0	6.26 ± 1.0
$A_{\|}$	-86.96 ± 2.0	-87.00 ± 2.0	-86.60 ± 1.0
$A_{\perp}$	-88.16 ± 2.0	-87.90 ± 2.0	-87.67 ± 2.0

Table 1. Spin-Hamiltonian parameters for Mn^{2+} in $Hg(ClO_4)_2 \cdot 6H_2O$ and in $Cd(ClO_4)_2 \cdot 6H_2O$ [5]. All crystal field and hyperfine parameters are in units of $10^{-4}\,cm^{-1}$.

with one [111] axis along the trigonal axis of the crystal, and it appears that at room temperature the octahedron is more perfect in $Cd(ClO_4)_2 \cdot 6\,H_2O$ and has an appreciable trigonal distortion in $Hg(ClO_4)_2 \cdot 6\,H_2O$.

The EPR spectrum of the system was studied from 77 to 298 K. As the crystal cools from toom temperature to liquid nitrogen temperature the value of b_2^0 increases slightly. But there was no change in the nature of the spectrum which can be associated with a possible phase transition of the host lattice. Dayal et al. [5], however, observed phase transitions in isostructural $Cd(ClO_4)_2 \cdot 6\,H_2O$ doped with Mn^{2+} at 272 ± 1 K and 115.5 ± 1 K. The value of b_2^0 in the Cd salt at 77 K was found to be $\approx 187.0 \times 10^{-4}\ \mathrm{cm}^{-1}$ [5], which is about four times the room temperature value. This indicates that at 77 K the trigonal distortion increases.

3.2. Doublet Separation of Forbidden Hyperfine Transitions

The intensity of the allowed lines is greatest for the magnetic field along or perpendicular to the three-fold axis. As the magnetic field deviates from these orientations, the intensity of the allowed lines decreases. At the same time a number of additional lines, corresponding to the forbidden hyperfine transitions $\Delta m = \pm 1$, appear. These transitions are well resolved for the electronic transition $M = +1/2 \to -1/2$. Figure 3 shows the allowed and forbidden hyperfine transitions in the electronic transition $M = +1/2 \to -1/2$. From the Figure it can be seen that the forbidden hyperfine transitions occur in pairs. The splitting is negligible for large values of θ. From the observed doublet separations in the electronic transition $M = +1/2 \to -1/2$ the axial component of the quadrupole coupling constant, Q', of the ^{55}Mn nucleus was calculated using the expression given in [7]. The best-fit value of Q' was found to be 0.0075 mT. The observed doublet separation $\Delta m = \pm 1$ and those calculated from the expression developed in [7] for the electronic transition $M = +1/2 \to -1/2$ are given in Table 2. The agreement between the calculated and observed values is fairly good.

Acknowledgements

The author is thankful to Professor Putcha Venkateswarlu of Indian Institute of Technology Kanpur for providing the experimental facilities for doing this work and to Minakshi Jain for helpful discussions.

Table 2. Observed and calculated doublet separation of the forbidden hyperfine transitions $\Delta m = \pm 1$ in the $M = +1/2 \to -1/2$ transition at $\theta = 12°$ and $Q' = 0.0075$ mT.

m	$H\|1/2, m+1\rangle \to \|-1/2, m\rangle - H\|1/2, m\rangle \to \|-1/2\ m+1\rangle$	
	Observed (mT)	Calculated (mT)
$-5/2$	1.70	1.70
$-3/2$	2.00	1.97
$-1/2$	2.28	2.24
$1/2$	2.55	2.51
$3/2$	2.81	2.79

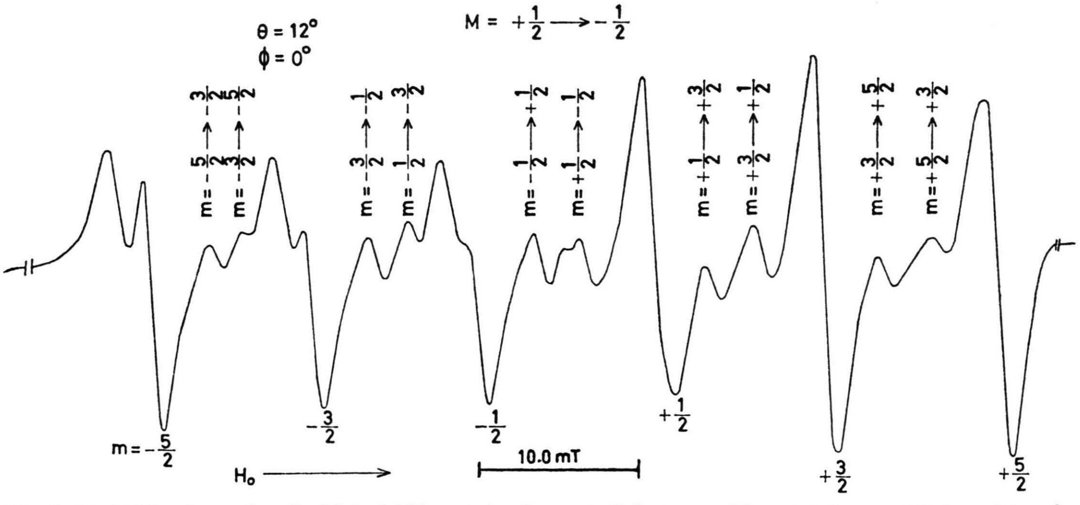

Fig. 3. Forbidden hyperfine doublets ($\Delta M = \pm 1$, $\Delta m = \pm 1$) between $M = +1/2 \to -1/2$ transition for H_0 making an angle 12° from the z-axis in $Hg(ClO_4)_2 \cdot 6\,H_2O{:}Mn^{2+}$ single crystals at 298 K. The unmarked lines are allowed transitions of other groups ($M = \pm 3/2 \to \pm 1/2$).

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