

PARAMAGNETIC RESONANCE OF  $Mn^{2+}$  IN  $SrS$ 

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The electron paramagnetic resonance spectrum of  $Mn^{2+}$  in the  $SrS$  crystal lattice is investigated. The constants of the spin Hamiltonian describing the observed spectrum are determined. The cubic field constant  $a$  is estimated from the anisotropic line broadening for the transitions  $M = \pm 3/2 \rightarrow \pm 1/2$  in powder. The spin-lattice relaxation time at room temperature,  $T_1 = 5 \times 10^{-8}$  sec, is determined from the difference in the width of the  $M = 1/2 \rightarrow -1/2$  transition lines at 300 and at 77° K. The low value of the hyperfine-structure constant  $A$  indicates that the coupling between the  $Mn^{2+}$  ions and the surrounding ions of the crystal lattice is of a covalent nature.

MANY investigators have studied in detail the paramagnetic resonance of  $Mn^{2+}$  ions in various crystals (see, for example, references 1-4). The ground state of  $Mn^{2+}$ ,  ${}^6S$ , has zero orbital momentum and to a first approximation is not split by a crystalline electric field. However, significant splittings of the energy levels by a crystalline field have been found in many crystals. These splittings are due to admixture of higher states, with non-zero orbital momentum, to the  ${}^6S$  state. The degree of admixture of states depends appreciably on the symmetry and magnitude of the crystal field.

The case of a cubic field is of considerable interest. Watanabe<sup>5</sup> has analyzed the splitting of the  ${}^6S$  state by a cubic field in detail theoretically, and has also compared his calculation with the existing experimental results for  $Mn^{2+}$  and  $Fe^{3+}$ . We should note, however, that although Watanabe's calculations agree qualitatively with the experimental data, there are in some cases considerable quantitative disagreements between the theoretical calculations and the experimental data.

We have investigated the paramagnetic resonance of  $Mn^{2+}$  in the  $SrS$  crystal lattice, which has cubic symmetry. The specimens studied were polycrystalline and contained about 0.05% of  $Mn^{2+}$  ions. The measurements were made at room temperature and at liquid nitrogen temperature at a

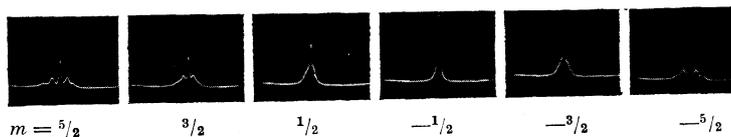
frequency  $\nu = 9,300$  Mc/sec. At both temperatures spectra consisting of six groups of lines with hyperfine structure (hfs) corresponding to the nuclear spin of  $Mn^{55}$ ,  $I = 5/2$ , were observed. Although the general nature of the spectrum did not differ appreciably at 300 and at 77° K, a narrowing of the lines and a small increase in the hfs constant were found on going from 300 to 77° K. Figure 1 shows the composition of the full spectrum, made up from oscillograms of the separate groups of hfs lines, photographed at 77° K.

The observed spectrum is described by the spin Hamiltonian

$$\hat{\mathcal{H}} = g\beta \mathbf{H}\hat{S} + A\hat{S}\hat{I} + \frac{1}{6}a[\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4 - \frac{1}{5}S(S+1)(3S^2-1)], \quad (1)$$

where the first term describes the interaction between an electron spin  $\mathbf{S}$  and the external magnetic field  $\mathbf{H}$ , the second — the interaction of an electron spin with the nuclear spin  $\mathbf{I}$  of  $Mn^{55}$ , and the third the interaction of an electron spin with the crystal field of cubic symmetry. Calculation by perturbation theory, taking into account third order terms in the hyperfine interaction and first order in the cubic field constant, leads to the following formula for the magnitude of the magnetic field strength at which absorption lines corresponding to the electron transitions  $M \rightarrow M-1$  would be observed:

FIG. 1. Paramagnetic resonance spectrum of  $Mn^{2+}$  in  $SrS$ , observed at 77° K. The magnetic field increases to the right.



$$\begin{aligned}
H = H_0 - Am - \frac{A^2}{2H_0} \{ & I(I+1) - m^2 + m(2M-1) \} \\
& + \frac{A^3}{4H_0} \{ [S(S+1) - M(M+1) \\
& + 2M(m-M)] [I(I+1) - m(m-1)] \\
& - [S(S+1) - M(M-1) + 2(M-1)(m-M+2)] \\
& \times [I(I+1) - m(m+1)] \} + F(a, M), \quad (2)
\end{aligned}$$

where

$$\begin{aligned}
H_0 = h\nu/g\beta, \\
F(a, M) = \begin{cases} 0 & \text{for the transition } M = 1/2 \rightarrow -1/2, \\ \pm 5/2 pa & \text{for the transitions } M = \pm 3/2 \rightarrow \pm 1/2, \\ \mp 2pa & \text{for the transitions } M = \pm 5/2 \rightarrow \pm 3/2, \end{cases} \\
p = 1 - 5\Phi, \quad \Phi = l^2 m^2 + l^2 n^2 + m^2 n^2
\end{aligned}$$

( $l$ ,  $m$  and  $n$  are the direction cosines of the angles which the external magnetic field makes with the cubic axes of the crystals).

As can be seen from (2), the second- and third-order shifts in the hyperfine structure are not the same for different electron transitions, as they depend on the magnetic quantum number  $M$ . The shifts produce splittings of every component of the hyperfine structure with a given nuclear magnetic quantum number into  $2S = 5$  ( $S$  is the electronic spin of  $Mn^{2+}$ ) lines, corresponding to different electronic transitions. From (2) it is seen that the magnitude of these splittings increases with increasing  $|m|$ .

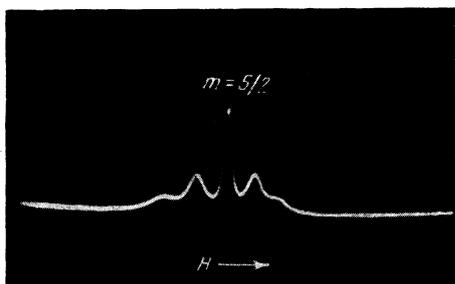


FIG. 2. The group of lines in the paramagnetic resonance spectrum of  $Mn^{2+}$  in  $SrS$ , corresponding to the nuclear magnetic quantum number  $m = 5/2$ . The central line of this group belongs to the electronic transition  $M = 1/2 \rightarrow -1/2$ . The arrow shows the direction of increasing magnetic field.

For the two extreme groups of lines corresponding to  $m = \pm 5/2$  (see Fig. 1), all five lines are well resolved. To show this more easily, the oscillogram of the group of lines with  $m = 5/2$  is reproduced in greater enlargement in Fig. 2. We notice that the splittings produced by the second order hfs shifts increase symmetrically from the center to the edges of the spectrum, while the third order shift leads to asymmetries of these splittings, as is seen in Fig. 1 especially clearly for the lines  $m = \pm 1/2$  and  $m = \pm 3/2$ .

Comparison of the observed spectrum with Eq. (2) gives the following values for the constants of the Hamiltonian:

$$\begin{aligned}
g = 2.0009 \pm 0.0005, \quad A = (75.4 \pm 0.2) \cdot 10^{-4} \text{ cm}^{-1}, \\
a < 1.4 \cdot 10^{-4} \text{ cm}^{-1} \quad \text{at } T = 300^\circ \text{ K};
\end{aligned}$$

$$\begin{aligned}
g = 2.0010 \pm 0.0005, \quad A = (77.0 \pm 0.2) \cdot 10^{-4} \text{ cm}^{-1}, \\
a < 1.2 \cdot 10^{-4} \text{ cm}^{-1} \quad \text{at } T = 77^\circ \text{ K}.
\end{aligned}$$

The signs of the constants  $A$  and  $a$  remain indeterminate. The identification of the lines in Fig. 1 with the quantum numbers  $m$  corresponds to a positive sign for  $A$ . The constants  $g$  and  $A$  were determined by comparing the positions of the lines  $M = 1/2 \rightarrow -1/2$ , which have the smallest width, with (2). In the best resolved group with  $m = 5/2$  the line width for  $M = 1/2 \rightarrow -1/2$  is 2.8 and 1.9 gauss at 300 and 77° K respectively, while the width for the lines  $M = \pm 3/2 \rightarrow \pm 1/2$  and  $M = \pm 5/2 \rightarrow \pm 3/2$  is 5.6 gauss at 300° K and 4.3 gauss at 77° K. The differences between the line widths for  $M = 1/2 \rightarrow -1/2$ ,  $M = \pm 3/2 \rightarrow \pm 1/2$  and  $M = \pm 5/2 \rightarrow \pm 3/2$  is connected with the anisotropic broadening produced by the random spread of the crystal field axes in the powder, and it follows from (2) that this is negligible for the lines  $M = 1/2 \rightarrow -1/2$ .

The cubic field constant  $a$  was determined from the anisotropic broadening of the lines  $M = \pm 3/2 \rightarrow \pm 1/2$ ,  $\Delta H_a \sim 5/2 \Delta pa$ , using for the maximum dispersion of  $p$  in the powder the value  $|\Delta p| = 1.25$  and estimating  $\Delta H_a$  from the difference in width of the lines  $M = \pm 3/2 \rightarrow \pm 1/2$  and  $M = 1/2 \rightarrow -1/2$ .

The lines  $M = \pm 5/2 \rightarrow \pm 3/2$  have roughly the same width as the lines  $M = \pm 3/2 \rightarrow \pm 1/2$ . This indicates that the crystal field in  $SrS$  has cubic symmetry, since in the case of a cubic field the anisotropic broadening for the lines  $M = \pm 5/2 \rightarrow \pm 3/2$  and  $M = \pm 3/2 \rightarrow \pm 1/2$  should be approximately the same, in that the frequency shifts, produced by a cubic crystal field, differ for these lines only by the factor  $(5/2 pa)/(2pa) = 5/4$ . The larger width of the lines  $M = 1/2 \rightarrow -1/2$  at room temperature than at 77° K is due to the contribution from the spin-lattice interaction. The spin-lattice relaxation time at room temperature, calculated from the difference between the widths of the lines  $M = 1/2 \rightarrow -1/2$  at room temperature and at liquid nitrogen temperature is  $T_1 = 5 \times 10^{-8}$  sec. As direct measurement of the spin-lattice relaxation time shows, the contribution from spin-lattice interaction to the line width at liquid nitrogen temperature is negligible.

The relative intensities of the lines  $M = \pm 5/2 \rightarrow \pm 3/2$ ,  $M = \pm 3/2 \rightarrow \pm 1/2$  and  $M = 1/2 \rightarrow -1/2$ , taking

their widths into account, agree with the theoretical ratio 5:8:9:8:5.

It is interesting to note that the magnitude of the hyperfine structure constant  $A$  for  $Mn^{2+}$  in SrS is considerably less than for  $Mn^{2+}$  in  $CaF_2$ .<sup>2</sup> This probably indicates the covalent character of the bonding of  $Mn^{2+}$  in SrS.

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