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Abstract. The $\Delta M = 2$ spin transitions are forbidden in first-order perturbation theory but allowed in the second order. With electron paramagnetic resonance, we have observed such transitions for Mn^{2+} in CaO between the $M = \frac{1}{2}$ and $M = +\frac{3}{2}$ levels between the $M = -\frac{3}{2}$ and $M = +\frac{1}{2}$ levels. The intensity dependence of these lines on the energy level spacing is in good agreement with theory. In addition, we have observed weaker lines due to transitions between $M = \pm\frac{1}{2}$ and $M = \pm\frac{5}{2}$ levels.

1. Introduction

Multiple quantum transitions [1–4] occurring in the presence of a strong microwave magnetic field between unequally spaced energy levels have been previously observed in the electron paramagnetic resonance (EPR) spectra of several ions in the alkaline earth oxides—namely, Ni^{2+}, Co^{+}, Fe^{2+} and Mn^{2+} in cubic magnesium oxide [5, 6]. Here, we report on $\Delta M = 2$ transitions of Mn^{2+} in CaO. We investigated in detail the intensity dependence of these lines on the inequalities of the energy level spacing (figure 1).

2. Theory

The relevant Hamiltonian for the Mn^{2+} ion in an octahedral environment is given by [7]

$$\boldsymbol{H}_0 = g\beta \boldsymbol{H} \cdot \boldsymbol{S} + \tfrac{1}{6}a\left[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5}S(S+1)\left(3S^2 + 3S - 1\right)\right] + A\boldsymbol{S} \cdot \boldsymbol{I} \qquad (1)$$

whee $\boldsymbol{S}$ and $\boldsymbol{I}$ are electron spin and nuclear spin operators. A is the hyperfine constant and a is the fine-structure constant. $\boldsymbol{H}$ is the magnetic field intensity. The nuclear Zeeman term has been omitted.

For the Mn^{2+} ion in CaO, $S = \frac{5}{2}$, $I = \frac{5}{2}$, $A = 81.7 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $a = 6 \times 10^{-4}\ \mathrm{cm}^{-1}$. The energy levels $E_{(M,m)}$ with $\boldsymbol{H}$ in the [100] direction are given as follows [7]. Here, M and m are the electron and nuclear spin quantum numbers.

$$E_{\pm1/2,m} = \pm\tfrac{1}{2}g\beta H + a \pm \tfrac{1}{2}Am + \left(A^2/2g\beta H_0\right)\left\{\pm\tfrac{35}{8} \mp \tfrac{1}{2} - \tfrac{17}{2}m\right\} \qquad (2)$$

$$E_{\pm3/2,m} = \pm\tfrac{3}{2}g\beta H - \tfrac{3}{2}a \pm \tfrac{3}{2}Am + \left(A^2/2g\beta H_0\right)\left\{\pm\tfrac{105}{8} \mp \tfrac{3}{2}m^2 - \tfrac{13}{2}m\right\} \qquad (3)$$

$$E_{\pm5/2,m} = \pm\tfrac{5}{2}g\beta H + \tfrac{1}{2}a \pm \tfrac{5}{2}Am + \left(A^2/2g\beta H_0\right)\left\{\pm\tfrac{175}{8} \mp \tfrac{5}{2}m^2 - \tfrac{5}{2}m\right\}. \qquad (4)$$

The usual EPR spectrum due to $\Delta M = 1$ transitions between levels consists of six groups of five lines. The fivefold splitting due to the fine structure proportional to a while the large sixfold splitting is generated by the hyperfine interaction proportional to A.

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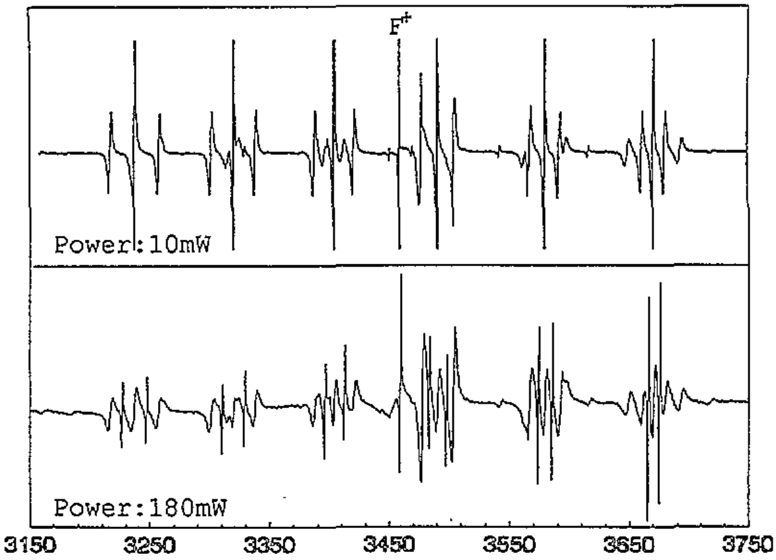

Figure 1. The spectra of Mn^{2+} obtained at both low and high microwave powers. The central sharp line corresponds to the F^+ centre. The temperature is 300 K.

From first-order time dependent perturbation theory the transition probability of an excited state l due to a $\Delta M = 1$ magnetic dipole transition from an initial state n is given by

$$\left|a_{nl}^{(1)}(t)\right|^2 = \left(g^2\beta^2H_1^2/4\hbar^2\right)\left|\langle l|S_+|n\rangle\right|^2\left|\left\{\exp\left[i\left(\omega_{ln}-\omega\right)t\right]-1\right\}/\left(\omega_{ln}-\omega\right)\right|^2 \tag{5}$$

and second-order perturbation yields for the transition probability of an excited state due to a $\Delta M = 2$ transition

$$\left|a_{nm}^{(2)}(t)\right|^2 = \left(g^4\beta^4H_1^4/16\hbar^4\right)\left|\langle m|S_+|l\rangle\right|^2\left|\langle l|S_+|n\rangle\right|^2/\left(\omega_{ln}-\omega\right)^2\left|\left\{\exp\left[i\left(\omega_{mn}-2\omega\right)t\right]\right.\right.$$
$$\left.\left.-1\right\}/\left(\omega_{mn}-2\omega\right)\right|^2 \tag{6}$$

where $S_\pm$ is the usual raising and lowering operator, H_1 is the microwave magnetic field at the sample and l is the intermediate state [8].

From the second-order perturbation theory, the transition from the E_n to E_m state is then allowed due to the presence of the intermediate state (l). The $\Delta M = 2$ transitions occur at microwave photon energies of half the energy separation between the m and n states. The corresponding magnetic field for a $\Delta M = 2$ transition lies halfway between the fields for n to l and l to m transitions.

First-order transition probability is proportional to H_1^2, while in second order it varies as H_1^4. Hence $\Delta M = 2$ transitions are only detectable at high microwave power levels. Also, the second-order transitions are proportional to $1/\Delta^2$, where $\Delta = \omega_{nl} - \omega$ (6).

3. Experimental details

The EPR spectra were taken with a Bruker Associates SRC 200 spectrometer operating at 9.76 GHz. The magnetic fields were read from this instrument's Hall probe to within ±10 μT. The sample temperature was controlled by an Air Products model DMX-1A/15 closed cycle refrigerator.

4. Results

Figure 1 displays the spectra of Mn^{2+} obtained at both low and high microwave powers. At low power only the $\Delta M = 1$ transitions are present while at high power these $\Delta M = 1$ lines display saturation effects. At high power, the narrow intense lines are due to $\Delta M = 2$ transitions. The variation in the intensity of the $\Delta M = 2$ transitions among the six hyperfine groups is noticeable. The second-order theory (6) predicts that the amplitude of the detected lines should be proportional to H_1^4/Δ^2, where

$$\Delta = \omega_{nl} - \omega = \frac{1}{\hbar}\left[\tfrac{1}{2}(E_m - E_n) - (E_l - E_n)\right] = \frac{1}{\hbar}\left[\tfrac{1}{2}(E_{1/2} - E_{-3/2}) - (E_{-1/2} - E_{-3/2})\right]$$
$$= -\frac{g\beta}{4\hbar}\left\{\frac{5a}{g\beta} - \frac{A^2}{2g^2\beta^2 H_0}(4m)\right\} = -\frac{g\beta}{4\hbar}(\Delta H). \qquad (7)$$

Here m are the nuclear spin quantum numbers and ΔH is the magnetic field separation between the $(M_{-3/2} \to M_{-1/2})$ and $(M_{1/2} \to M_{3/2})$ transitions.

According to equation (7) the amplitude of the detected $\Delta M = 2$ lines should be proportional to $1/(\Delta H)^2$. In figure 2, the line intensities observed for $\Delta M = 2$ transitions for various nuclear quantum numbers (m) are plotted as a function of $1/(\Delta H)^2$. ΔH values for various m were determined experimentally from the magnetic field values for relevant single quantum transitions. The $\Delta M = 2$ intensity for $m = -\frac{5}{2}$ transition was set equal to unity. The observed line intensity ratios are in agreement with the predicted values.

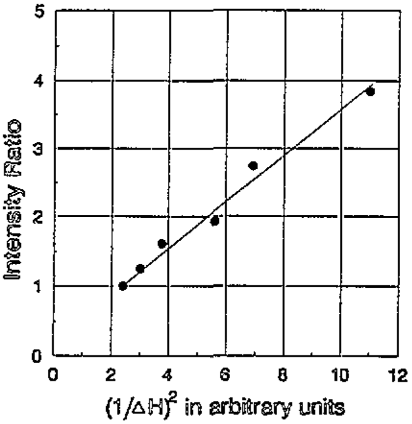

Figure 2. The relative $\Delta M = 2$ intensity ration against $1/(\Delta H)^2$ for various m in figure 1. Filled circles are experimentally observed intensity ratios. The solid line is the ratio predicted by $I \propto 1/(\Delta H)^2$.

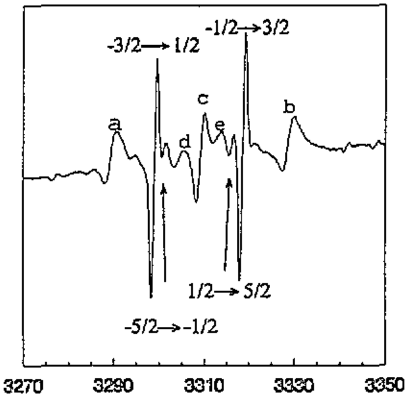

Figure 3. EPR transitions of the $m = -\frac{3}{2}$ pentad: microwave power, 190 mW; temperature, 13 K. $\Delta M = 1$ transitions are a, $M = -\frac{3}{2} \to M = -\frac{1}{2}$, b, $M = \frac{1}{2} \to M = \frac{3}{2}$, c, $M = -\frac{1}{2} \to M = \frac{1}{2}$, d, $M = \frac{3}{2} \to M = \frac{5}{2}$, and e, $M = -\frac{5}{2} \to M = -\frac{3}{2}$. $\Delta M = 2$ transitions are as marked.

Measured values of the magnetic fields for relevant single quantum transitions were also used to predict the positions of $\Delta M = 2$ lines for the $m = -\frac{3}{2}$ pentad. As predicted by the second-order perturbation theory, the corresponding magnetic field for a $\Delta M = 2$ transition lies halfway between the fields for relevant single quantum transitions (figure 3). All the transitions are well resolved for this particular pentad. Weak $\Delta M = 2$ transitions $M_{1/2} \to M_{5/2}$ and $M_{-5/2} \to M_{-1/2}$ are also evident.

5. Conclusion

Our results for double quantum transitions of Mn^{2+} in CaO are in good agreement with predictions from second-order time dependent perturbation theory [8].

In addition to the strong $\Delta M = 2$ transitions between $M = \pm\frac{1}{2}$ and $M = \pm\frac{3}{2}$ levels of the Mn^{2+} ion, we have detected weaker double quantum transitions between $M = \pm\frac{1}{2}$ and $M = \pm\frac{5}{2}$ levels. These weaker transitions were not detectable for Mn^{2+} in MgO [8].

The phenomena of double quantum transitions may be very helpful in resolving an overlap EPR spectrum.

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