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Formation of $Mn^{2+}Cd_m$ ($m \geq 10$) in Mn^{2+}-CdO which is treated in CS_2 at 700°C: An observation by ESR

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When CdO which contained dilute Mn^{2+} was treated in CS_2 at 700 °C, a new hyperfine splitting was observed in the ESR of the Mn^{2+} ion. The spectrum consists of six groups of ESR lines, each of which consists of more than 20 lines. The intensity ratio of these lines, when plotted against the magnetic field distance from the central peak position, approximately coincides with the calculated intensities based on the assumption that 10 or 11 Cd nuclei are equally interacting with the electronic system of Mn^{2+}. Such a structure is formed when gas-phase CdS interacts with Mn^{2+}. These results suggest that a new type of magnetic semiconductor $MnCd_mS_{m+1}$ ($m \geq 10$) may be formed if MnS and CdS, with the ratio of 1:10 or 1:11, are deposited from the vapor phase onto a solid surface.

INTRODUCTION

The ESR of the Mn^{2+} ion has been studied by many researchers and many reports have appeared in this and other journals. Title, Huang, and others measured the coupling constant of $^{55}Mn^{2+}$ in various crystal matrices.[1-8] Huang, Young, Simanek and others investigated the temperature dependence of $^{55}Mn^{2+}$. Kikuchi, Lambe, van Wierigen, Title, and Dorain studied $^{55}Mn^{2+}$ when the host crystal was Cds or CdSe.[7,11-13] Title and Matsumura studied the relation between the bond ionicity and $^{55}Mn^{2+}$.[11,14] Dorain and Ludwig detected some superhyperfine structure in the ESR spectra of Mn^{2+}.[13,15] Title, Ludwig, Rauber, and others studied the ESR spectra of some $3d^5$ ions, Fe^{3+},[4,16,17] and Cr^{+} (Refs. 4, 15, and 18), which are isoelectronic with Mn^{2+}.

The Cd hyperfine splitting observed in this work has not been reported in any of the surveyed literature with the exception of Dorain,[13] who reported a superhyperfine structure having a line separation of 82 μT. This value is approximately 50% of the value of the line separation observed in the present work, which is, therefore, a new finding.

EXPERIMENTAL PROCEDURE

The CdO used was a reagent of Wako Pure Chemical Co. 1.0 g of CdO was placed in a porcelain boat and was heated in an atmosphere of CS_2, approximately 13 Pa, at 700°C for 30 min. Some 70 wt. % of the CdO was converted to CdS. After cooling, the ESR spectrum was recorded in air. The CdO reagent used contained a small amount of Mn (approximately 0.1% as MnO_2) and therefore it was not necessary to add Mn ions to it intentionally. If another 0.1% of MnO_2 was mixed with it and resulting mixture ground in an electric ball mill for 1 h, the ESR spectrum obtained after CS_2 processing had a larger linewidth. Since the Fe^{3+} ion has $3d^5$ electrons and is isoelectronic with Mn^{2+}, 1.4 mg of $Fe(NO_3)_3 \cdot 9H_2O$ was mixed with 1.0 g of CdO and was ground by an electric ball mill for 40 min. This mixture was then heated in CS_2 as described above. Another approach, starting with CdS, was also made. 1.0 g of MnO_2 was added to 1.0 g of CdS (High Purity Chemical Co.) and was ground by an electric ball mill for 30 min. This mixture was then reduced in a H_2 atmosphere (0.1 Pa) at 400 °C for 30 min. ESR spectra were recorded at 20 °C using a JES-ME3X–type spectrometer, with 100-kHz modulation frequency. Measurements of liquid-nitrogen temperature were also carried out using a quartz Dewar vessel in which the sample tube was immersed during measurements. Visible-light irradiation of the sample was made by a JCR 100-V, 150-W –type halogen lamp (Iwasaki Electric Co.) which was connected to a light-guide cable SLS-150 (Sumita Optics Co.).

RESULTS

The ESR spectrum recorded at 20 °C is shown in Fig. 1; the spectrum obtained at liquid-nitrogen temperature was similar. One of the six ESR peaks, the one appearing

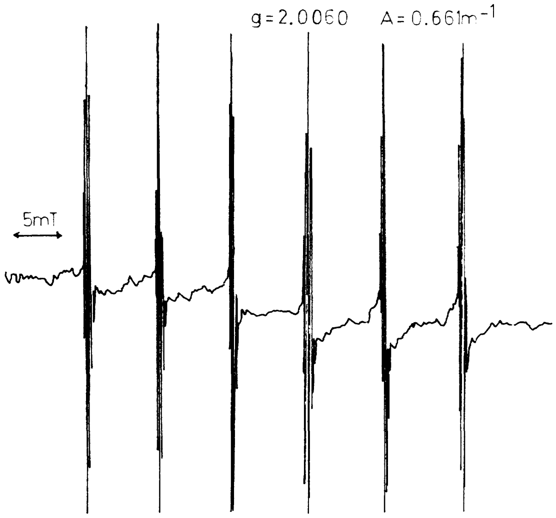

FIG. 1. The ESR spectrum of CdO treated in CS_2. The CdO contains a small amount of Mn ions.

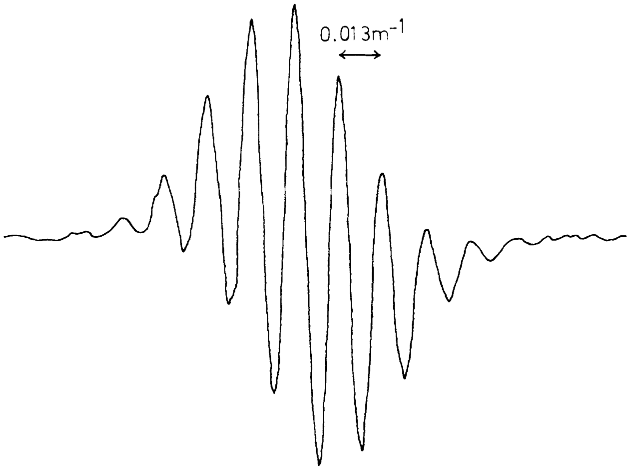

FIG. 2. The magnified ESR spectrum of Mn^{2+} in CdS-CdO corresponding to the lowest-field peak of the six lines.

at the lowest magnetic field value, is enlarged to provide more detail, as shown in Fig. 2. If the sample tube was irradiated with visible light, the amplitude of the ESR signal decreased to 91% of the dark signal. The MnO_2-CdS sample reduced in H_2 at 400 °C gave a six-line Mn^{2+} ESR spectrum without any additional hyperfine structures. The g factor was 2.0051 and the splitting constant was 0.668 m^{-1}, values which are almost identical with those of the spectrum in Fig. 1. The sulfurized (Fe^{3+}-CdO system gave a broad ESR spectrum with no hyperfine structure.

DISCUSSION

It is well known that the Mn^{2+} (^{55}Mn isotope 100%) ion gives a six-line ESR spectrum having a g factor close to 2.000.[19,20] Many metallic oxides which contain a small amount of Mn ions as impurity, if treated in a CS_2 atmosphere at 700 °C, give Mn^{2+} ESR spectra having a g factor close to 2,000, but having different splitting constant values.[21]

The hyperfine structure observed in Figs. 1 and 2 is caused by the Cd nuclei. There are two naturally occurring Cd nuclei which have a nuclear-spin magnetic moment, namely ^{111}Cd and ^{113}Cd. The abundances are 12.8% and 12.2%, and magnetic moment values are -0.59 and -0.61, respectively. Considering that the full width at half maximum of the first-derivative curve in Fig. 2 is 40% of the line separation, the 3.3% difference in the magnetic moment values cannot be resolved. Therefore, the magnetic moment value is approximately -0.60, and the natural abundance of the magnetic nuclei is 25%. The remaining 75% nuclei are magnetically inactive. If a Mn^{2+} has spin nuclear coupling with only one Cd ion, the resulting spectrum will have 18 component lines, because each of the six lines splits into three lines, as shown in Fig. 3(a). If a Mn^{2+} ion couples with two Cd ions, each of the six lines will split into five lines, as shown in Fig. 3(b). If this procedure is repeated, the intensity ratio can be calculated for the number of equally interacting Cd ions, n. The results for $n = 2-14$ are shown in Fig. 4.

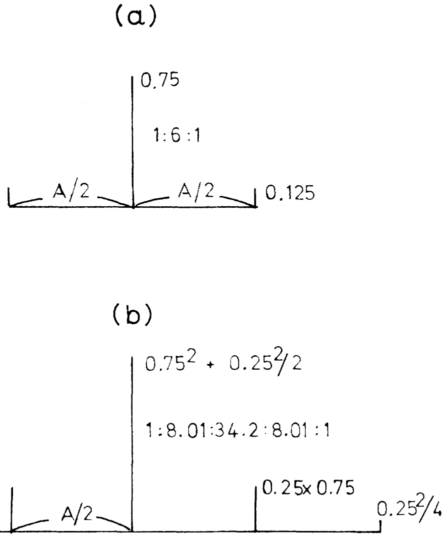

FIG. 3. The calculated intensity ratios in the ESR hyperfine structure of the Mn^{2+}-Cd and Mn^{2+}-Cd_2 systems. (a) Coupling with only one cadmium nucleus. (b) Coupling with two cadmium nuclei. A is the coupling constant. The abundance of the combination of the Cd nuclei (111 or 113), when both have no magnetic moment is 0.75^2, the abundance when one has the magnetic moment is $2 \times 0.25 \times 0.75$, and the abundance when both have the magnetic moment is 0.25^2.

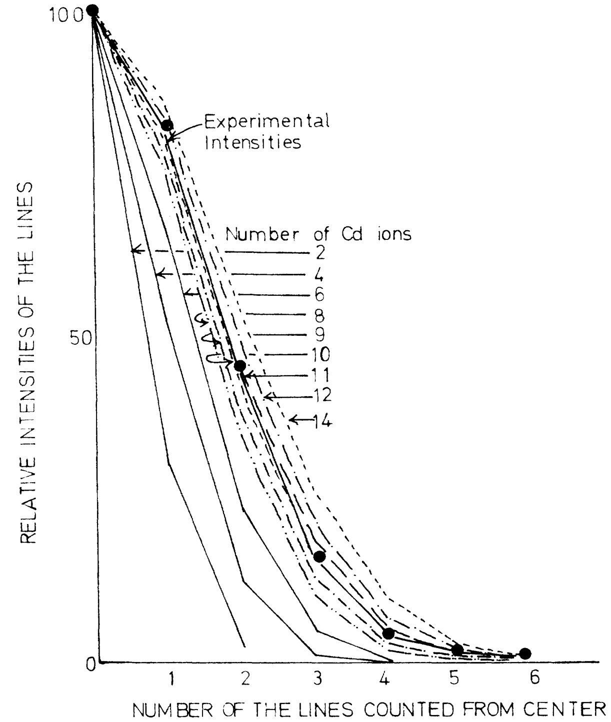

FIG. 4. The calculated and experimental intensity ratios of the hyperfine-component lines when the number of coupling Cd nuclei is varied in the calculated intensities.

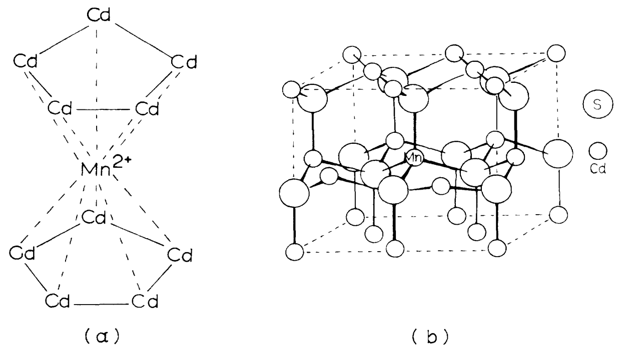

FIG. 5. (a) One of the possible models which may interpret the ESR spectrum obtained, $Mn^{2+}Cd_{10\ \mathrm{or}\ 11}$. (b) One of the possible models which may interpret the ESR spectrum obtained, $Mn^{2+}Cd_{12}S_4$.

The experimental intensity ratio corresponds to $n = 10$ or 11. Therefore, if the current assumption, "all the Cd ions are coupling with the Mn^{2+} ion equally" is correct, the number of Cd ions coupling with the Mn^{2+} ions is 10 or 11. However, it might be possible that some additional lines will be found or resolved in the future. Therefore, it would be more proper to say that the number of the cadmium nuclei equally interacting with the Mn^{2+} ion is 10 or 11, or perhaps more.

The molecular model which interprets the ESR spectra, Figs. 1 and 2, may be either (a) or (b) in Fig. 5. In (a), Cd^{2+} directly coordinates to Mn^{2+}. In (b), Mn^{2+} replaces one of the Cd^{2+} positions in the hexagonal crystal lattice (wurzite).[22] In (b), there are 12 equivalent Cd^{2+} ions with respect to the Mn^{2+} ion under consideration. In this case, one of the Cd^{2+} ions will be missing as a result of crystal-defect formation. In structure (b), the covalent bonds Mn—S—Cd must be formed. This then will lead to a shift of g factor from that of a free-electron value, because, in one of the excited-state orbitals, the unpaired electron of Mn^{2+} will have spin densities on the sulfur atom and, therefore, the λLS operator will have a nonvanishing term. If $-382\ \mathrm{cm}^{-1}$ is used as λLS,[23] the shift of the g factor will be somewhat larger than 2.0060. For this reason structure (b) is less likely.

The mechanism for generating $Mn^{2+}\text{-}Cd_{10\ \mathrm{or}\ 11}{}^{2+}$ will correspond to one of the schemes (1)–(3) in Fig. 6. In (1), CdS, whose sublimation point is 980 °C in N_2, will sublimate at 700 °C and 13 Pa. Therefore, the Mn^{2+} ions should be surrounded by CdS molecules. In (2), MnS will occupy a CdS defect in the crystal lattice of CdS. This, considering that the melting point of MnS is 1530 °C and the sublimation pressure of MnS is not high enough at 700 °C, is not likely to occur. In (3), Mn^{4+} in the CdS lattice is reduced by two electrons derived from the gas-phase CS_2. The ESR spectrum obtained by the CdS, to which MnO_2 was added and which was then reduced in H_2, did not have the hyperfine structure of Cd nuclei.

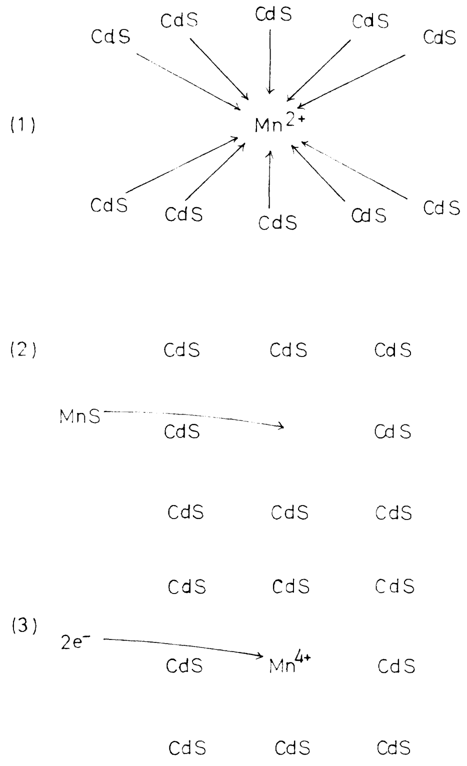

FIG. 6. Three schemes which may generate a Mn-Cd complex spin-coupling system. (1) CdS, which has sublimated, coordinates to Mn^{2+}. (2) MnS, which has sublimated, enters a CdS defect. (3) Two electrons from a CS_2 molecule reduce a Mn^{4+} ion in the CdS lattice.

Therefore, our conclusion is that the species consistent with Figs. 1 and 2 is either $(Mn^{2+}Cd_{10}S_{10})S$ or $Mn^{2+}Cd_{10\ \mathrm{or}\ 11}{}^{2+}$.

The reduction in intensity of the ESR spectrum when irradiated by visible light is due to some kind of polarized structure such as $Mn^{3+}\text{-}Cd^{+}$ or $Mn^{+}\text{-}Cd^{3+}$.

In spite of the number of papers already published, the type of Cd hyperfine splitting overlapped with Mn splitting has not been detected until now. The reason lies in the method of diffusing Mn^{2+} ions into the host crystal. The essential point seems to be the reaction of Mn^{2+} with vapor-phase CdS. The reaction condition of Dorain[13] was 1770 °C, at which temperature vapor-phase CdS may react with Mn^{2+}. Our conclusion, derived from this work, is that a new paramagnetic species, $Mn^{2+}Cd_{10\ \mathrm{or}\ 11\ (\mathrm{or\ more})}$ is formed in the Mn^{2+}-CdO treated in CS_2, and that the Cd hyperfine-splitting constant is $0.013\ \mathrm{m}^{-1}$. The results of the present report suggest that, if we can establish an experimental condition by which both MnS and CdS deposit on a solid surface from a gas phase with a ratio of 1:10 (or 1:11), a new magnetic semiconductor $MnS(CdS)_{10\ \mathrm{or}\ 11}$ may be produced.

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