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EPR of Mn^{2+} in $CdGa_2S_4$ and in $CdGa_2Se_4$; Influence of Covalent Bonding on the Parameters of the Spin-Hamiltonian

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(Z. Naturforsch. **27 a**, 1624—1633 [1972]; received 10 August 1972)

The EPR-spectra of Mn^{2+} in $CdGa_2X_4$ (X=S, Se) single crystals were measured and described by a Spin-Hamiltonian with an axial and with a cubic crystal field component:

$D = -(225.3 \pm 0.2) \cdot 10^{-4}\,cm^{-1}$ and $a = (6.6 \pm 0.2) \cdot 10^{-4}\,cm^{-1}$ for $CdGa_2S_4$;
$D = -(919.3 \pm 0.3) \cdot 10^{-4}\,cm^{-1}$ and $a = (15 \pm 2) \cdot 10^{-4}\,cm^{-1}$ for $CdGa_2Se_4$.

The g-values $g_{\parallel} = 2.0012 \pm 0.0005$, $g_{\perp} = 2.0016 \pm 0.0010$ for $CdGa_2S_4$ and $g_{\parallel} = 2.0029 \pm 0.0005$, $g_{\perp} = 2.0039 \pm 0.0010$ for $CdGa_2Se_4$ are slightly different from those of the binary chalcogenides CdX (X=S, Se).

The hyperfine constants A, $-(64.0 \pm 0.3) \cdot 10^{-4}\,cm^{-1}$ for $CdGa_2S_4$ and $-(60.7 \pm 0.3) \cdot 10^{-4}\,cm^{-1}$ for $CdGa_2Se_4$ are nearly the same as those of the equivalent binary cadmium chalcogenides. It is shown that all parameters of the cadmium chalcogenides are characterized by the covalent part of the bonding. The g-values can be explained by an interaction of the 3d orbitals of Mn^{2+} with the ligand orbitals. The hyperfine constant is caused by an interaction of the excited 4s-Mn^{2+} states with the ligand states. By optical absorption measurements the value of the band gap in $CdGa_2X_4$ (X=S, Se, Te) is determined.

1. Introduction

The binary chalcogenides of cadmium, CdX (X = O, S, Se, Te) are known as semiconducting materials. The chemical bond in these substances is assumed to be of partial covalent character. Numerous spectroscopic investigations on the Cd-chalcogenides have been performed (UV-, IR-absorption, EPR) and relations between the spectroscopic parameters and the character of the chemical bond in these solids were proposed. The investigations on the binary chalcogenides of cadmium are reviewed by AVEN and PRENER [1].

The ternary chalcogenides of the type $A^{2+}B_2^{3+}X_4^{2-}$ form quite an interesting group of solids: A = Cd, Zn, Hg; B = Al, Ga, In; X = O, S, Se, Te. Many of these compounds crystallize with the $CdGa_2S_4$-structure. In this structure the metal atoms A^{2+} and B^{3+} are tetrahedrally coordinated by the chalcogen atoms. The structure is very similar to the zincblende structure and therefore interesting informations may be expected by comparing the binary and the ternary cadmium chalcogenides.

The chalcogenides $CdGa_2X_4$ (X = S, Se, Te) are isotypic and crystallize within the space group $S_4^2 - I\bar{4}$ with two formula units in the elementary cell as shown by HAHN et al. [2]. Single crystals of these materials can be grown by vapour phase transport reaction [3]. The purpose of the present work is to determine the parameters of the EPR-Spin-Hamiltonian of Mn^{2+} in $CdGa_2X_4$:Mn^{2+} (X = S, Se, Te) and to compare these values with the corresponding values of Mn^{2+} in CdX:Mn^{2+} (X = S, Se, Te) from literature. A better knowledge about the chemical bond in the semiconducting chalcogenides can be expected from such an investigation. Accompanying optical absorption measurements in the UV- and visible region have been done too.

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* Dissertation D 17, Darmstadt 1971.

2. Experimental

Single crystals of the ternary cadmium-gallium chalcogenides were grown from the vapour phase by transport reaction, using iodine as transport gas. Cd, Ga, S, Se, Te, with a purity of 99.999% have been used as starting materials. For EPR measurements a part of the cadmium within the crystals was substituted by manganese. For doping the crystals during the growth, Mn metal powder was added to the charge. The concentration of Mn^{2+} in the crystals, according to the added amount of Mn, was varied between 0.05 and 5 at.%. The crystals had dimensions up to $(2\times4\times10)$ mm^3 for $CdGa_2S_4$, $(2\times2\times8)$ mm^3 for $CdGa_2Se_4$, and $(1\times2\times4)$ mm^3 for $CdGa_2Te_4$. The colour of the crystals is yellow, red, and black, respectively.

For the most part the crystals had the shape of needles with a triangular cross section. By rotating the crystals around their needle axis in an optical two-circle-goniometer, the angles between the normal axes of the crystal prism planes were determined. The analysis of these angles proved that the needle axis of the crystals is the crystallographical [110]-axis (or one of the other axes of this zone: $[\bar{1}10]$, $[1\bar{1}0]$, $[\bar{1}\bar{1}0]$). This is in agreement with the EPR-spectra.

By X-ray powder analysis it was verified that the crystals had the tetragonal structure proposed by HAHN et al.[2]. The values of the lattice constants were determined. Together with the values of HAHN et al.[2] they are given in Table 1. The cadmium and the gallium ions are surrounded by chalcogen tetrahedra in such a way that each sulphur ion belongs simultaneously to one tetrahedron around a cadmium ion and to two tetrahedra around gallium ions (Fig. 1). The ordering of Cd-ions and Ga-ions creates a superstructure (a doubling of the c-axis) with respect to the zincblende lattice.

For the EPR measurements an AEG-20X-spectrometer was used. The clystron frequency was measured with an Hewlett-Packard digital counter via a microwave frequency converter. The magnetic field was measured with an AEG-proton resonance unit. The maximum error in the determination of the resonance from the spectra is estimated ±2 Oe. EPR-measurements in the temperature region $100\,\mathrm{K}\leqq T\leqq600\,\mathrm{K}$ were performed with an AEG variable temperature accessory. At the temperatures of the liquid helium, a Varian V 4500 – 10 A EPR-spectrometer was used.

For the EPR measurements the crystals were fastened to a quartz rod which was fixed on a goniometer head. The crystal was adjusted experimentally on the quartz rod by the use of an optical two-circle goniometer. Two crystal axes have been selected as rotational axes for the experiments: a) the $[1\bar{1}0]$-axis, equivalent to the rotation of H_0 in the $(1\bar{1}0)$-plane; and b) the [001]-axis, equivalent to the rotation of H_0 in the (001)-plane.

For the optical absorption measurements the crystals were fastened on quartz glass, so that one of the prism planes of the crystal was parallel to the quartz plate. The crystals were then graded and polished to plates of about 0.3 mm thickness. A monochromator M4 QII and a detector PM QII (Zeiss) were used for the determination of the absorption spectrum in the range $200\,\mathrm{nm}\leqq\lambda\leqq1000\,\mathrm{nm}$.

3. Results

The total information on the angular dependence of the Mn^{2+}-EPR spectrum is available from the rotation of H_0 in the $(1\bar{1}0)$- and (001)-planes. In Fig. 2 and in Fig. 3 the angular dependence of the Mn^{2+}-spectrum at room temperature in a $CdGa_2S_4$ crystal doped with 0.5 at.% Mn^{2+} is shown for these two rotations. The Mn^{2+}-spectrum can be described by the Spin-Hamiltonian:

$$\begin{aligned}\mathcal{H}=&\,g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)\\&+D[S_z^2-\tfrac{1}{3}S(S+1)]\\&+\tfrac{1}{6}a[S_z^4+S_y^4+S_x^4-\tfrac{1}{5}S(S+1)(3S^2+3S+1)]\\&+A\boldsymbol{S}\boldsymbol{I}.\end{aligned}\qquad(1)$$

x, y, z correspond to the crystallographic axes [100], [010], [001]. The g-tensor is expressed by $g_{\parallel}$ (g-value in the direction $z\triangleq[001]$) and $g_{\perp}$ (g-value in the direction of $x\triangleq[100]$ or $y\triangleq[010]$). S is the electron spin of Mn^{2+} ($S=5/2$) with the components of the spin operator S_x, S_y, S_z. β is the Bohr magneton. D is the axial, a is the cubic crystal field splitting parameter, and A is the hyperfine

Table 1. Lattice constants of the ternary chalcogenides $CdGa_2X_4$ (X=S, Se, Te).

Crystal	Valus of HAHN et al.[2]						Own Values		
	a/Å	c/Å	c/a	x/a	y/a	z/c	a/Å	c/Å	c/a
$CdGa_2S_4$	5.57_7	10.0_8	1.80_8	0.27	0.26	0.14	5.54 ±1	10.16 ±2	1.83 ±2
$CdGa_2Se_4$	5.7_4	10.7_3	1.87_0	0.25	0.26	0.13	5.743±5	10.757±5	1.873±2
$CdGa_2Te_4$	6.0_9	11.8_1	1.93_8	0.27	0.26	0.13	6.110±5	11.841±5	1.938±2

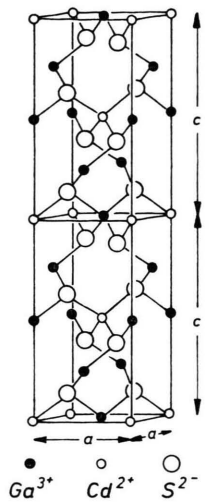

Fig. 1. Unit cell of $CdGa_2S_4$.

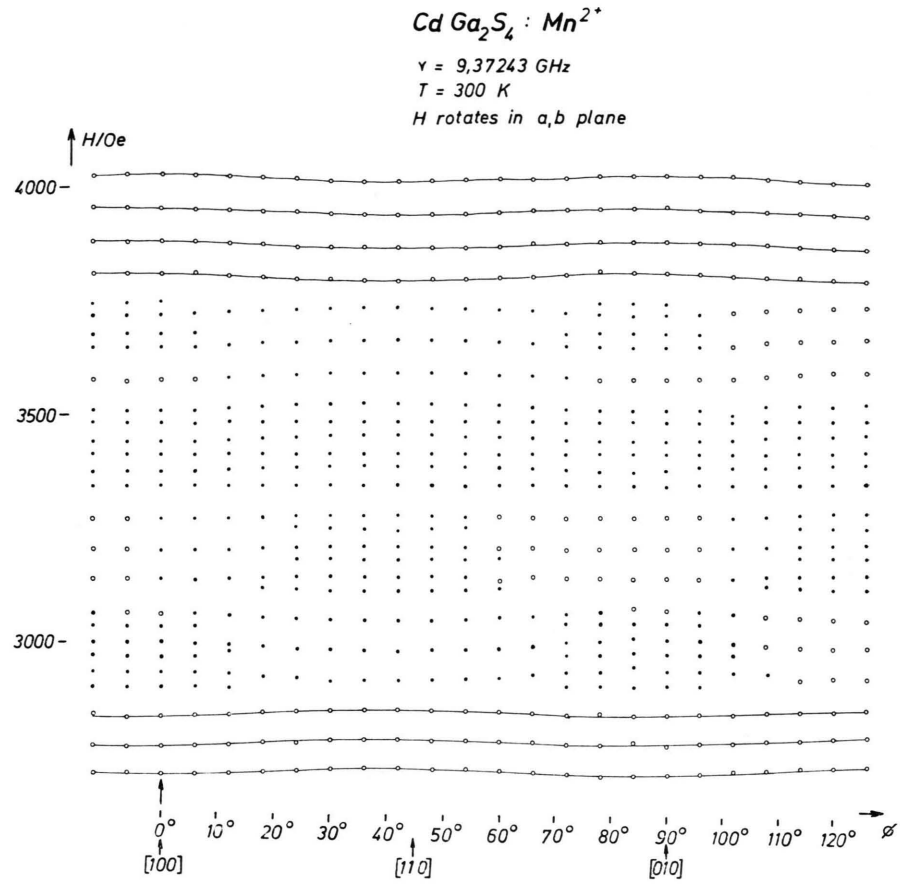

Fig. 3. The angular dependence of the Mn^{2+}-EPR-lines in $CdGa_2S_4$ (0.5 at.% Mn). H_0 rotates in the (001)-plane ($\triangleq$ *a*, *b*-plane) of the crystal. The filled in circles are resonance values which could not be taken from the spectrum very precisely because of an overlap of several resonance lines. The lines drawn are the resonance values calculated from the Hamiltonian [Equation (1)].

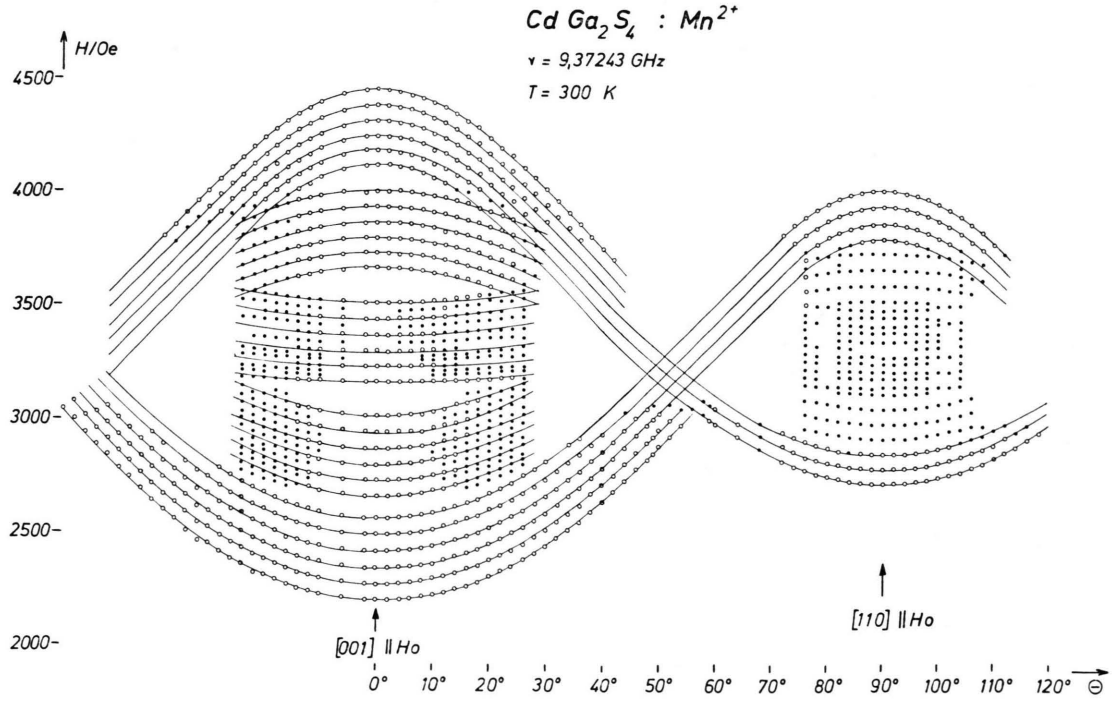

Fig. 2. The angular dependence of the resonance fields of Mn^{2+} in $CdGa_2S_4$ (0.5 at.% Mn). The magnetic field rotates in the $(1\bar{1}0)$-plane. The filled in circles are resonance values which could not be taken from the spectrum very precisely because of an overlap of several resonance lines. The lines drawn give the resonance values calculated from the Hamilton [Equation (1)].

Table 2. The EPR-parameter values and the optically determined band gap values of $CdGa_2X_4$ (X=S, Se, Te) and of CdX (X=S, Se, Te).

Crystal	Space Group	T/K	ν/GHz	g	$D/10^{-4}\,cm^{-1}$	$a/10^{-4}\,cm^{-1}$	$A/10^{-4}\,cm^{-1}$	Ref.	E/eV
CdS	$C_{6v}^4-P6_3mc$	300	9	2.0020 ± 5	8.3 ± 1		-65.3 ± 1	a	2.58 d
CdSe	$C_{6v}^4-P6_3mc$	77	9	2.0041 ± 5	15.6 ± 1		-62.2 ± 1	a	1.84 d
CdTe	$T_d^2-F\bar{4}3m$	20	9	2.0075 ± 10		27 ± 2	-57.1 ± 4	b	1.60 d
$CdGa_2S_4$	$S_4^2-I\bar{4}$	300	9	$g_{\parallel}=2.0012\pm5$	-225.3 ± 2	6.6 ± 2	-64.0 ± 3	c	3.2 c
				$g_{\perp}=2.0016\pm10$					3.5 e
$CdGa_2Se_4$	$S_4^2-I\bar{4}$	300	9	$g_{\parallel}=2.0029\pm5$	-919.3 ± 3	15 ± 2	-60.7 ± 3	c	2.3 c
				$g_{\perp}=2.0039\pm10$					2.4 e
$CdGa_2Te_4$	$S_4^2-I\bar{4}$	2–300	9	—	—	—	—	c	1.5 c

a J. SCHNEIDER, S. R. SIRCAR, and A. RÄUBER, Z. Naturforsch. **18a**, 980 [1963].
b T. P. P. HALL, W. HAYESAND, and F. I. B. WILLIAMS, Proc. Phys. Soc. London **78**, 883 [1961].
c This work.
d B. RAY, II–VI Compounds, Pergamon Press, Oxford, London 1969, p. 54.
e J. A. BUEN, R. NITSCHE, and M. LICHTENSTEIGER, Physica **27**, 448 [1961].

splitting constant. The parameters were calculated by a parameter fitting program ** in which the energy matrix is solved by the Jacobi method.

The values of the parameters are listed in Table 2, together with the corresponding values of the binary chalcogenides.

The sign of the crystal field splitting parameter D was determined by the measurement of the temperature dependence of the resonance intensity and was found to be negative. Consequently, the other signs of the parameters of the Spin-Hamiltonian could be determined.

With the X-band frequency all transitions $\Delta M_S=1$ of Mn^{2+} in $CdGa_2S_4$:Mn^{2+} are observable for all orientations Θ, Φ of the crystal with respect to H_0. For Mn^{2+} in $CdGa_2Se_4$:Mn^{2+} the crystal field splitting has reached an amount comparable in magnitude to the X-band frequency. Consequently, the transition $M_S=-5/2\rightarrow M_S=-3/2$ is not observed in the Mn^{2+}-EPR spectrum of $CdGa_2Se_4$:Mn^{2+} for $H_0\parallel[001]$. This is explained by the energy level diagram for $H_0\parallel[001]$ as shown in Figure 4 a. For a crystal orientation of $H_0\parallel[110]$ six fine structure lines were measured in this crystal. This can be understood from Figure 4 b, which gives the fine structure energy levels for $H_0\parallel[110]$. The energy levels of Fig. 4 a and Fig. 4 b were calculated by an appropriate computer program using the parameter values given in Table 2.

** This program is a modification of the QCPE 69-IBM-Program of H. H. GLADNEY and is developed by Dr. W. J. BECKER. The program is in the library of the "Deutsches Rechenzentrum", 61 Darmstadt, BRD.

We have been unable to observe a Mn^{2+}-EPR spectrum in single crystals of $CdGa_2Te_4$, doped with Mn^{2+}, in the temperature range $4.2\,K\leqq T\leqq 300\,K$. The reason for this fact is not yet clear.

The line width ΔH of the Mn^{2+}-EPR spectrum in $CdGa_2S_4$ as a function of temperature and of Mn^{2+} concentration was studied earlier [4]. It was shown that ΔH is determined by magnetic interactions of

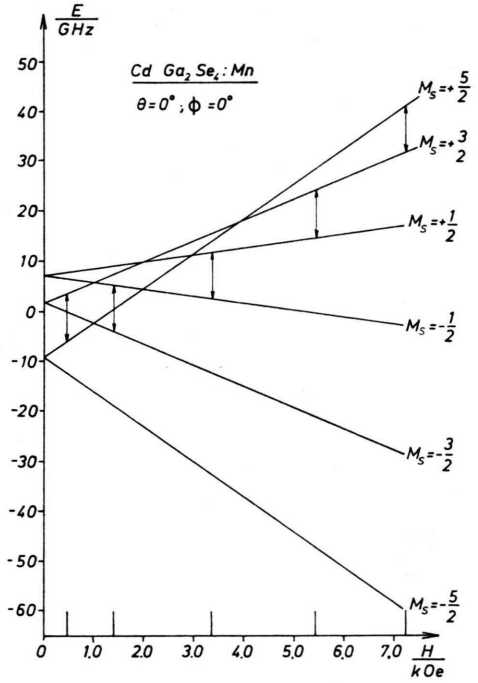

Fig. 4 a. Energy levels (fine structure) of Mn^{2+} in $CdGa_2Se_4$: Mn^{2+} for $H_0\parallel[001]$.

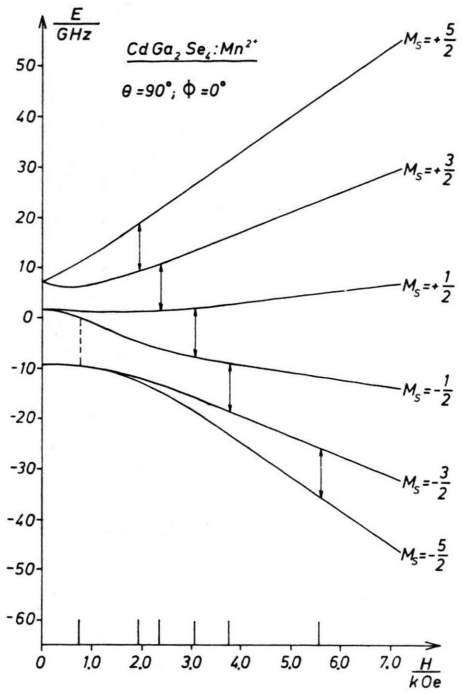

Fig. 4 b. Energy levels (fine structure) of Mn^{2+} in $CdGa_2Se_4 : Mn^{2+}$ for $H_0 \parallel [100]$.

the Mn^{2+} ion with the nuclear spins of the gallium isotopes as long as the concentration of Mn^{2+} is smaller than 0.5 at.%. The g-values of $CdGa_2S_4:Mn^{2+}$ given in Ref. [4] are too low.

The band gaps of the ternary chalcogenides, determined by the optical absorption measurements are 3.2 eV for $CdGa_2S_4$, 2.3 eV for $CdGa_2Se_4$, and 1.5 eV for $CdGa_2Te_4$. The energy values are given for $I/I_0 = 0.5$ of the absorption curve at the band edge.

In Fig. 5 the optical absorption spectrum of a $CdGa_2S_4$-crystal doped with 1 at.% Mn^{2+} relative to a crystal of $CdGa_2S_4$, not doped with Mn^{2+}, is plotted together with the absorption curves of $CdGa_2S_4$ and of $CdGa_2S_4:Mn^{2+}$, respectively.

Ascribing the broad absorption peak at 400 nm to a Mn^{2+} absorption implies that the manganese ions in the $CdGa_2S_4$ crystal are energetically very near the valence band. The first excited state of the Mn^{2+} ion in the crystal is the conduction band of the crystal. The distance between the $^6S - Mn^{2+}$ ground state and the conduction band of the crystal is about 3.2 eV ($= 26\,000\ cm^{-1}$) which is very near to the energy distance $^6S - {}^4P$ of the free Mn^{2+} ion.

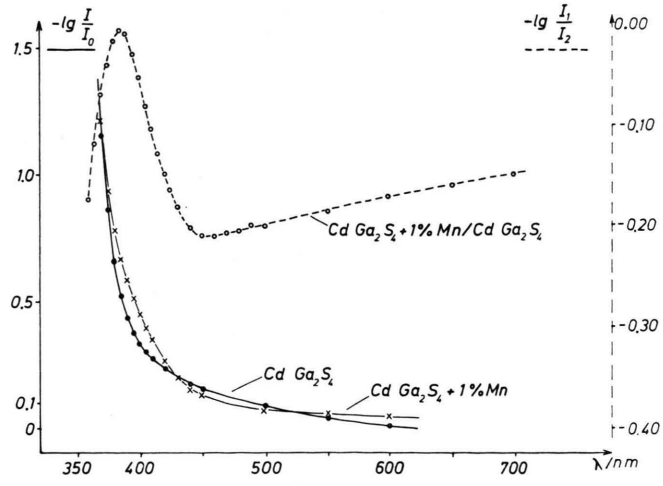

Fig. 5. The optical absorption of $CdGa_2S_4$ (●) and of $CdGa_2S_4$ doped with 1 at.% Mn (×) as a function of wavelength. The dashed curve (○) shows a measurement of $I_1/I_2 = I_{CdGa_2S_4:Mn^{2+}}/I_{CdGa_2S_4}$.

4. Discussion

The basis of the discussion is the assumption of Mn^{2+}-ions on the Cd-sites in $CdGa_2X_4$. This assumption is made for the following reasons:

1. The valency of the ions favours a Mn^{2+} on the Cd^{2+} site.

2. In tetrahedral coordination the ionic radii of the Mn^{2+}, Cd^{2+}, and Ga^{3+} are 0.85 Å, 0.96 Å, and 0.58 Å, respectively. It may be assumed that the Mn^{2+} ion rather substitutes the Cd^{2+}, having a volume larger than Mn^{2+}, than the Ga^{3+} having a volume smaller than Mn^{2+}.

3. The fact that the hyperfine constants of Mn^{2+} in $CdGa_2X_4$ (X = S, Se) do not differ from the hyperfine constants of Mn^{2+} in other crystals of similar covalence as in CdX (X = S, Se) (see Table 2) shows that Mn^{2+} is situated at a Cd-lattice site and is not on an interstitial site.

4.1. g-Values and the MO-Model

In a pure ionic crystal the g-shift $\Delta g = g - 2.0023$ is explained by an admixture of the excited ^4P-state into the ^6S-ground state of the Mn^{2+} ion. WATANABE [5] as well as GABRIEL et al. [6] calculated for this interaction a shift $\Delta g \approx -0.0004$, in agreement with the experimental values in ionic crystals. In the binary cadmium chalcogenides Δg-values, positive and large compared to the ionic value $\Delta g = -0.0004$, have been found. This effect is explained by a co-

valent mixing of the orbitals of the paramagnetic S-state ion with the orbitals of the ligands. FIDUNE and STEVENS [7] showed that for these covalent admixtures two cases are to be discussed (see Fig. 6).

a) The energy of the ground state of the undisturbed ligand ion is lower than the energy of the ground state of the undisturbed central ion. The ground state I (see Fig. 6 a), caused by the interaction between the ligand states and the states of the central ion is in this case dominantly characterized by the ligand orbitals. An excitation of an electron from the bonding orbital (I) to the non-bonding (II) or anti-bonding (III) orbitals can be interpreted as a charge transfer from the ligands to the central ion. In this case a positive Δg is expected.

b) The ground state of the undisturbed ligand ion is energetically higher than the ground state of the undisturbed central ion. The new ground state I (Fig. 6 b) is in this case mainly characterized by the orbitals of the central ion. An excitation of an electron from the ground state I to the states II and III can be understood as a charge transfer from the central ion to the ligands. A negative Δg is expected in this case.

WATANABE [8] gives a quantitave calculation of Δg for this covalent mixing of the orbitals. By a linear combination of ligand p-functions, special ligand functions for a σ-bond to the central metal ion are built up. These ligand functions are mixed with the 3d-functions of the metal ion. Only orbitals of the same symmetry can be mixed.

For a tetrahedral complex the MO-orbitals for the ligands Mn^{2+} complex are:

$$|t_2^b, i\rangle = \sqrt{1-\alpha^2}\ |d(t_2, i)\rangle + \alpha\,|\mathrm{Li}(t_2, i)\rangle,$$
$$|t_2^a, i\rangle = \alpha\ |d(t_2, i)\rangle - \sqrt{1-\alpha^2}\,|\mathrm{Li}(t_2, i)\rangle,$$

with $i = x, y, z$; a = antibonding, b = bonding.

Herein the $|d(t_2, i)\rangle$ are the 3d functions of the central ion, with the symmetry (t_2, i). $|\mathrm{Li}(t_2, i)\rangle$ characterizes the ligand function combined to give the symmetry (t_2, i). α is the admixture parameter. $\alpha = 0.5$ characterizes pure covalent bonding, $\alpha = 0$ and $\alpha = 1$ pure ionic bonding, between the central ion and the ligands. For these states Watanabe calculated a g-shift of

$$\Delta g = \pm \tfrac{8}{5} \varrho_d \left[\{1 - \alpha^2 + \alpha \sqrt{1-\alpha^2} \cdot S\} \frac{1}{\Delta E^n} + \{\alpha^2(1-\alpha^2) + \alpha \sqrt{1-\alpha^2} \cdot (2\alpha^2 - 1)\, S\} \frac{1}{\Delta E^a} \right] \quad (2)$$

neglecting matrix elements estimated to be smaller than the overlap integral S. For the definitions of ΔE^n and ΔE^a see Figure 6. ϱ_d is the spin-orbit coupling constant of the 3d electrons. For a charge transfer, as defined above, from the ligands to the central ion more than five electrons are in the orbitals of the excited configuration and these orbitals are mainly of 3d character. The spin orbit coupling constant of the many electron state is positive and Δg is positive (case a). For a charge transfer from the central ion to the ligand the number of 3d electrons in the excited configuration is less than five. Here the spin-orbit coupling constant of the many electron system is negative, Δg is negative (case b). For Mn^{2+} in CdX (X = S, Se, Te) the measured positive g-shifts indicate that we have a charge transfer from the ligand anions to the central ion (case a). The charge transfer increases from the sulphur to the tellurium anions.

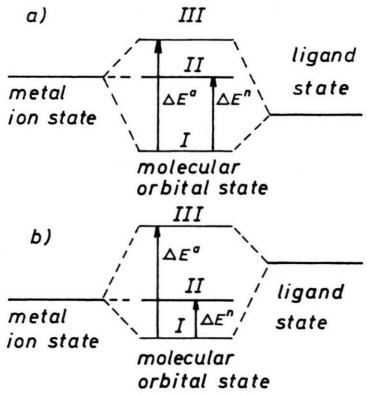

Fig. 6. The molecular orbital energy scheme for an interaction of the central ion with the orbitals of the ligands. a) The energy state of the undisturbed metal ion is energetically higher than the energy state of the undisturbed ligands. b) The energy state of the undisturbed metal ion is energetically lower than the energy state of the ligands.

The g-shift of Mn^{2+} in $CdGa_2S_4$ is more negative than could be explained by an ionic $^4P - {}^6S$ interaction within the Mn^{2+} ion. The optical measurements prove that the energetic distance between the $Mn^{2+} - {}^6S$ ground state and the next excited state (the conduction band) is about the same as the distance between the $Mn^{2+} - {}^6S$-state and the $Mn^{2+} - {}^4P$-state (26 000 cm^{-1}) which would give the ionic g-shift $\Delta g \approx -0.0004$. A Δg caused by an interaction between this excited state of Mn^{2+} in $CdGa_2S_4 : Mn^{2+}$ and the ^6S ground state therefore would not much exceed $\Delta g = -0.0004$.

The negative Δg of Mn^{2+} in $CdGa_2S_4$ can be understood assuming a mixture of the Mn^{2+} ground state with the ligand ground states in such a way

that there is a charge transfer from the central ion to the ligands (case b). To calculate Δg by use of Eq. (2) ΔE^{n}, ΔE^{a}, S, and the admixture coefficient α must be known. For small covalencies ($\alpha \to 0$), neglecting the term with $1/\Delta E^{a}$ because $\Delta E^{a} > \Delta E^{n}$, and with the realistic assumption $S \approx 0.2$ [8], Eq. (2) may be approximated by

$$\Delta g = \pm \tfrac{8}{5} \varrho_{d} \frac{1}{\Delta E^{n}} (1 - \alpha^{2}). \qquad (2\,a)$$

The optical absorption measurements of a Mn^{2+} doped $CdGa_2S_4$ crystal have shown that Mn^{2+} is energetically very near to the valence band of the crystal. Therefore ΔE^{n} is approximately the band gap of the crystal.

In a first approximation we take $\alpha = \text{const}$ within the Cd-chalcogenides:

$$\Delta g = \pm \tfrac{8}{5} \varrho_{d} \frac{1}{\Delta E} \text{ const}. \qquad (2\,b)$$

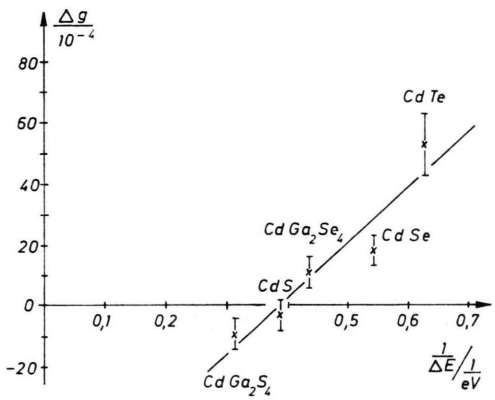

Fig. 7. Δg as function of $1/\Delta E$, ΔE being the band gap from optical absorption measurement. The g value of Mn^{2+} in $CdGa_2X_4$ (X=S, Se) is the isotropic mean value of $g_{\parallel}$ and $g_{\perp}$ in these substances (from Table 1).

In Fig. 7 Δg is plotted as a function of $1/\Delta E$, where ΔE is the optically measured band gap of the crystal (Table 2). Fig. 7 proves that the relation given by Eq. (2 b) is a good approximation of the g-shift of Mn^{2+} in the binary and ternary Cd-chalcogenides.

4.2. *g-Values and Covalence Model*

A widely used qualitative parameter to discuss the chemical bond is PAULING's [9] covalence parameter c. This parameter is based on PAULING's electronegativity scale, and the covalence of the bond between two atoms A and B with the electronegativities X_A and X_B is given by the empirical relation (HANNAY and SMITH [10]):

$$c = 1 - 0.16(X_A - X_B) - 0.035(X_A - X_B)^2. \qquad (3)$$

Many authors tried to establish a correlation between the parameters of the Spin-Hamiltonian of Mn^{2+} in various host lattices and PAULING's covalence parameter c of the bond Mn – X. A review of these works is given by TITLE [11, 12].

The electronegativity values X as used here, are those given by GORDY and THOMAS [13]: $X_{Mn} = 1.4$, $X_{Ga} = 1.5$, $X_{Cd} = 1.5$, $X_S = 2.5$, $X_{Se} = 2.4$, $X_{Te} = 2.1$.

To receive the covalence of the bond Mn – X (X = S, Se, Te) the values of c, calculated by Eq. (3), are divided by the number n of the ligands (for tetrahedra $n = 4$). The result is:

$$\text{Mn – S: } c/n = 19.5\%; \quad \text{Mn – Se: } c/n = 20.1\%; \quad \text{Mn – Te: } c/n = 21.8\%.$$

In Fig. 8 a graph is presented, where the Δg values for Mn^{2+} in the binary and in the ternary cadmium chalcogenides are given as a function of c/n in analogy to the discussion of TITLE [12]. The plot $\Delta g = f(c/n)$ shows that for different substances with a covalence of about 20% $\Delta g = \Delta g(c)$ can be described to a first approximation by one parameter c, calculated by Equation (3). However it may be concluded that $c_{\text{binary}} \neq c_{\text{ternary}}$ within the cadmium chalcogenides. Equation (3) is developed only for binary bonds. The interaction beyond the next neighbours is neglected herein.

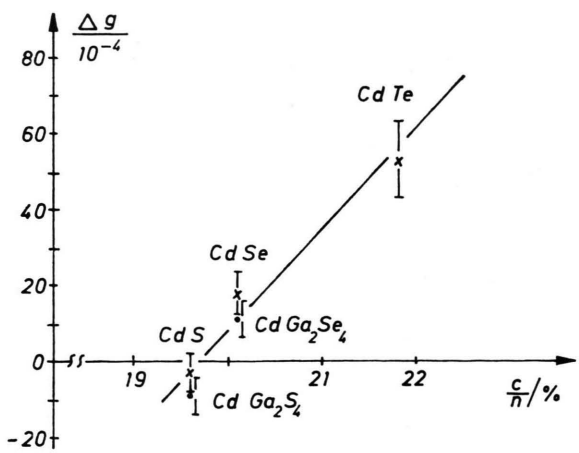

Fig. 8. The g shift of Mn^{2+} in CdX (×) (X=S, Se, Te) and in $CdGa_2X_4$ (●) (X=S, Se) as a function of the covalence values c/n. The g value of Mn^{2+} in $CdGa_2X_4$ (X=S, Se) is the isotropic mean value of $g_{\parallel}$ and $g_{\perp}$ in these substances.

In the binary and in the ternary cadmium chalcogenides as well the Mn^{2+} ion is surrounded by a chalcogen tetrahedron. Thus the difference between the Δg values of $CdX:Mn^{2+}$ and of $CdGa_2X_4:Mn^{2+}$ can be caused only by the additional Ga^{3+} ion in the ternary compounds.

In the binary chalcogenides the bond $Mn-X$ is not purely ionic and the manganese ion Mn^{2+} gives part of its electron charge back to the sulphur ion. This "charge transfer" from the manganese to the ligands causes a positive Δg [case a) of the MO-model]. As the difference in the electronegativity between manganese and the chalcogens decreases from sulphur to tellurium, the bond becomes more covalent and the charge transfer from the manganese to the chalcogen increases. Therefore Δg becomes more positive (see Figure 8). In the case of $CdGa_2S_4$ the difference in the electronegativities between the gallium atom and the sulphur atom is less than the difference between the Mn atom and the sulphur atom, so that the bonding $S^{2-}-Ga^{3+}$ is less ionic than the bonding $Mn^{2+}-S^{2-}$. This means that the Ga^{3+} ions draw away a larger amount of charge from the S^{2-} ion than the Mn^{2+} does. The sulphur atom has a relatively high electronegativity and therefore, the sulphur ion S^{2-} does not intend to give electrons easily to the neighbouring atoms. Consequently, the charge transfer from the S^{2-} ion to the Ga^{3+} ion is partly compensated by a charge transfer from the Mn^{2+} ion to the S^{2-} ion. This should result in a negative Δg value [case b) of the MO-model]. In $CdGa_2Se_4$ the electronegativity of the selenium is less than the electronegativity of the sulphur and therefore the charge transfer to the Ga^{3+} ion does not need to be compensated by the Mn^{2+} ion. The g-shift of Mn^{2+} in $CdGa_2Se_4$ is positive. For $CdGa_2Te_4$ the low electronegativity of tellurium should allow a charge transfer from the Te^{2-} ion not only to the Ga^{3+} ion, but to the Mn^{2+} ion as well. An increased positive Δg is expected in this case.

The discussion proves that the relative change of Δg within the system CdX and within the system $CdGa_2X_4$ can be explained by PAULING's covalence c, at least qualitatively.

PAULING's electronegativities characterize the chemical behaviour of binary bonds $A-B$. A use of these values in substances, where the orbitals of more than two different atoms overlap might not give reliable values for the covalence. Here the use of the concept of electronegativity should only be regarded as a method to facilitate the understanding how the spectroscopic parameters change within a group of isostructural substances, but not as a method to receive reliable Δg values or similar spectroscopic parameters.

To gain more accurate covalence values for different substances more refined methods have been developed. For instance, PHILLIPS [14] proposed a covalence scale by using the experimentally determined values of the band gap and the nearest neighbour distance d. Since this method implies the knowledge of further spectroscopic parameters, it is evident that these spectroscopically determined covalence values give a better relation between c and other spectroscopical parameters than can be received with PAULING's covalence scale calculated from the electronegativities of the elements only. Instead of using these more refined covalence values, we do think that the use of the spectroscopic parameter ΔE in connection with the MO model is preferable (see Chapter 4.1).

4.2. The Crystal Field Splitting Constants D and a

To explain the crystal field splitting constants D and a of S-state ions, a number of model is discussed in the literature. A review of the work done in this field is given by SHARMA et al. [15–17]. WYBOURNE [18] and VAN HEUVELEN [19] showed that the use of relativistic eigenfunctions for the ions might be essential in discussing the crystal field interactions. By semi-empirical methods they calculated D values for Mn^{2+} in ionic crystals ($-90\cdot10^{-4}$ cm^{-1}), in the right order of magnitude. A disagreement was found for D values of crystals, where a large amount of covalent bonding is present.

The D values of Mn^{2+} for $CdGa_2X_4:Mn^{2+}$ ($-225.3\cdot10^{-4}$ cm^{-1}, and $-919.3\cdot10^{-4}$ cm^{-1}, for $CdGa_2S_4$ and $CdGa_2Se_4$, respectively) are much larger than the D value of Mn^{2+} estimated by VAN HEUVELEN for a typical ionic crystal. We conclude that in the chalcogenides the D value is characterized by the covalent part in the bond. This is supported by the following facts: The axial splitting constant D is proportional to A_2^0 (see for instance [20]), the amplitude of the axial crystal field component. A_2^0 is a function of the chalcogen tetrahedron. The coordinates of the chalcogen ions determined by X-ray diffraction are not sufficiently accurate to determine the distortion of the chalcogen tetrahedron. If we assume that the distortion of the chalcogen tetrahedron is proportional to the difference between the c/a values found and $c/a=2$ (see Table 1) – there are two different chalcogen

tetrahedra stacked in the [001]-direction of the unit cell – we expect, with the value $(c/a)_S = 1.83$ and $(c/a)_{Se} = 1.87$, the following relations

$$(A_2^0)_S > (A_2^0)_{Se} \text{ and } |D_S| > |D_{Se}| \text{ respectively.}$$

The indices S and Se stand for $CdGa_2S_4$ and $CdGa_2Se_4$.

The experimental values (Table 2) show the opposite relation. The more covalent selenide has a larger D value than the less covalent sulfide. The same relation is found for the cubic crystal field parameter in the binary [11] and in the ternary chalcogenides:

$$a_{CdGa_2S_4} = 6.6 \cdot 10^{-4}\ cm^{-1} < a_{CdGa_2Se_4} = 15 \cdot 10^{-4}\ cm^{-1},$$

$$a_{CdS} = 3.3 \cdot 10^{-4}\ cm^{-1} < a_{CdSe} = 14.3 \cdot 10^{-4}\ cm^{-1}.$$

This indicates that the covalent admixtures of the ligand orbitals with the 3d Mn^{2+} electrons determine the crystal field parameter in the Spin-Hamiltonian.

The conclusion is in agreement with the results of NICHOLSON and BURNS [20], who measured the nuclear quadrupole coupling constant $e^2 q Q$ of various nuclei in different crystals and compared these values with the splitting constant D of Mn^{2+} in the same crystals doped with Mn^{2+}. The nuclear quadrupole moment is independent of the crystal field and of the outer electrons. Therefore, $e^2 q Q$ should be directly proportional to A_2^0. If the EPR parameter D is related to A_2^0 by: $D = \text{const } A_2^0$, we expected $e^2 q Q = f(D)$.

NICHOLSON and BURNS found that $e^2 q Q$ could not be connected with D by any continuous function. This leads to the conclusion that D is essentially determined by the change of the 3d functions caused by the orbital interaction with the ligand functions.

4.3. The Hyperfine Constant A

The dependence of the hyperfine splitting constant A of Mn^{2+} in various crystals as a function of PAULING's covalence value c/n has been discussed by different authors [12, 21–24]. The A values of Mn^{2+}

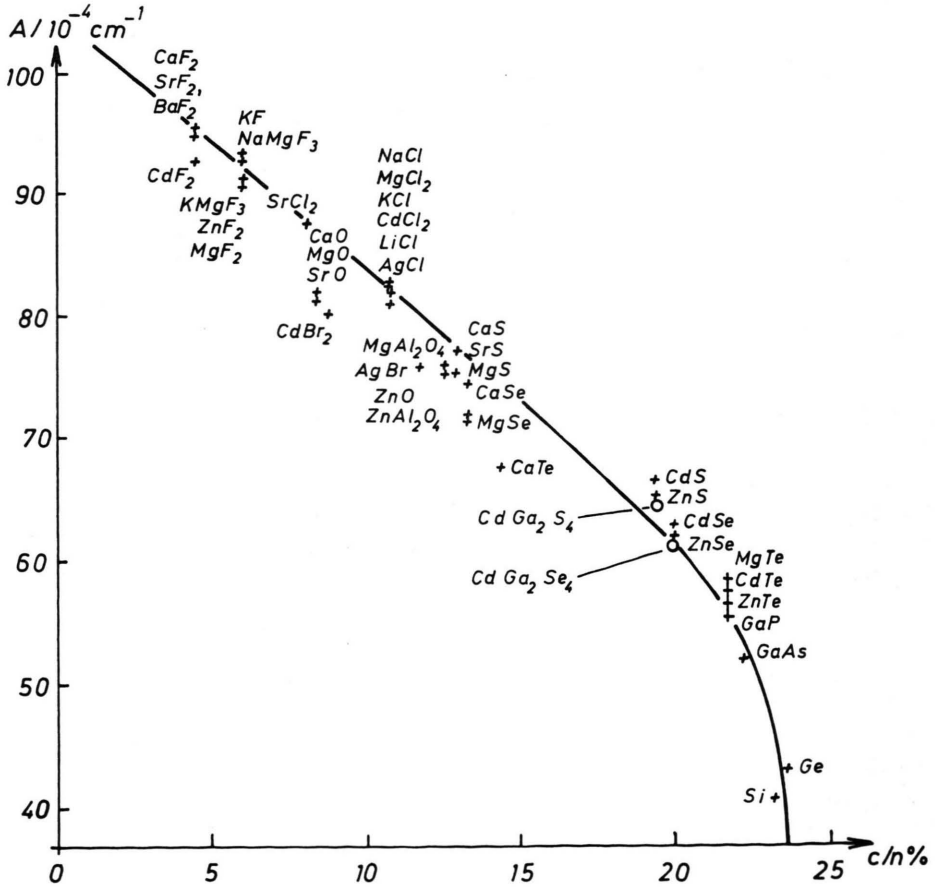

Fig. 9. The hyperfine splitting constant A of Mn^{2+} in various host lattices as a function of the covalence c/n. The values are taken from a paper by SIMANEK and MÜLLER [24]. o: this paper.

in $CdGa_2S_4$ ($-64.0\cdot10^{-4}$ cm^{-1}) and in $CdGa_2Se_4$ ($-60.7\cdot10^{-4}$ cm^{-1}) fit quite well the empirical relation $A=f(c/n)$ (Figure 9). Furthermore they nearly agree with the corresponding values of the binary chalcogenides CdS ($-66.6\cdot10^{-4}$ cm^{-1}) and CdSe ($-62.2\cdot10^{-4}$ cm^{-1}) (see Table 2 and Figure 9). Two different models are discussed in the literature to explain the dependence $A=f(c/n)$: For Mn^{2+} in ZnF_2 IKENBERRY and DAS [25] have shown that the influence of the covalent character of the bond on the hyperfine constant A can be explained by an exchange polarisation of the inner Mn^{2+} electron shell with the 3d functions.

SIMANEK and MÜLLER [24] ascribe the essential part of the dependence of A on the covalence of the bonding to an overlap of the partly occupied $Mn^{2+}-4s$ orbital with the ligand orbitals. By the Fermi-contact-interaction the 4s electrons would cause a change of the hyperfine splitting.

The results of the EPR measurements of Mn^{2+} in the ternary chalcogenides support the model of SIMANEK and MÜLLER: The g-shift of Mn^{2+} in the ternary and in the binary chalcogenides changes the sign within this class of compounds. This fact can be explained by an overlap of the 3d functions with the ligand functions.

Since the A values of the ternary chalcogenides are nearly the same as those of the binary chalcogenides, we assume that the 3d functions do not cause the dependence of A on the covalence (as they do for the g-shifts). Another mechanism might be significant for the dependence $A=f(c/n)$, such as the overlap of the 4s electrons with the ligand functions.

5. Conclusions

The EPR spectra of Mn^{2+} in single crystals of $CdGa_2S_4$:Mn^{2+} and of $CdGa_2Se_4$:Mn^{2+} are measured and described. The parameters of the Spin-Hamiltonian are compared with those of Mn^{2+} in the binary chalcogenides CdX:Mn^{2+} (X = S, Se, Te). The discussion shows that in the binary and ternary chalcogenides the parameter values are not primarily determined by the interatomic distances within the crystals, but by the covalence of the bonding. The bond is characterized by the overlap of the ligand orbitals with the 3d orbitals (in the case of the g-shift) and with the excited 4s orbitals (in the case of the hyperfine constant A). The discussion is extended by relating the EPR parameters to PAULING's covalence parameter c, determined by the electronegativities of the elements. Thus the negative g-shift in $CdGa_2S_4$ and the Δg values for the binary and the ternary chalcogenides can be understood. However, PAULING's covalence parameter gives only a rough picture of the bonding within the cadmium chalcogenides. A relation

$$\Delta g=\Delta g(1/\Delta E)$$

as given by WATANABE [5] from MO calculations fits quite well the experimental Δg values of Mn^{2+} within the cadmium chalcogenides.

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