SPIN-LATTICE COEFFICIENTS OF Mn^{2+} IN II-VI COMPOUNDS ☆

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The spin-lattice coefficients of Mn^{2+} in CdTe and ZnTe have been measured. Our data allow us to evaluate the random stress distribution within the samples. Our results are compared with values obtained for Mn^{2+} in MgO and CaO.

The study of the spin-lattice coupling contributes to the understanding of the mechanisms that produce the splitting of the energy levels of ions in crystals. The spin-lattice coefficients which characterize this interaction have been previously determined [1–4] for 3d and 4f S-state ions in cubic crystals, by measuring the shifts induced by an external uniaxial stress on the electron paramagnetic resonance (EPR) spectral lines.

In this letter we report measurements of the spin-lattice coefficients of Mn^{2+} in the II-VI wide-tap semiconductors CdTe and ZnTe. These compounds have a zincblend structure where the Mn^{2+} ions substitutionally occupy the tetrahedrally coordinated metal sites.

The samples were single crystals grown by a modified Bridgman technique, and doped with 0.05 at% of Mn^{2+}. They were cut into the shape of rectangular prisms with their edges parallel to the [110] direction. The orientation was controlled by X-ray diffraction techniques and the errors found to be smaller than 1°. The experiments were performed using a 35 GHz spectrometer [5], applying uniaxial stresses up to 700 kg/cm^2 in the [110] direction and rotating the magnetic field H in the perpendicular plane.

The Mn^{2+} ground state is ($3d^5$, ${}^6S_{5/2}$) and the appropriate zero-order spin Hamiltonian for the local cubic symmetry is:

$$H_0 = g\beta \boldsymbol{H}\cdot\boldsymbol{S} + A\boldsymbol{I}\cdot\boldsymbol{S} + \\ + \frac{1}{6}a\,[S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S^2+3S-1)]$$

At 77K the values determined for the giromagnetic factor g, the hyperfine constant A and the cubic crystal field parameter a were, for CdTe:

$$g = 2.0067(5); A = -57.3(2)\times 10^{-4}\ \mathrm{cm}^{-1};$$

$$3a = +88.9(9)\times 10^{-4}\ \mathrm{cm}^{-1}$$

and for ZnTe:

$$g = 2.0106(5); A = -56.5(2)\times 10^{-4}\ \mathrm{cm}^{-1};$$

$$3a = +92.2(9)\times 10^{-4}\ \mathrm{cm}^{-1},$$

these values being in excellent agreement with previous determinations [6–8]. The parameters were found to be only weakly dependent with temperature.

The spin lattice interaction is described by a spin Hamiltonian H_{sl} where second and fourth order terms

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Table 1.
Spin lattice coefficients in units of cm^{-1}

	CdTe	ZnTe	MgO [1]	CaO [2]
G_{11}	$+0.46 \pm 0.01$	$+0.80 \pm 0.03$	$+1.5$	$+0.48$
G_{44}	-0.51 ± 0.01	-0.36 ± 0.02	-0.30	-0.10

are allowed in the spin variables. Only the former terms have been observed in uniaxial stress experiments so that the Hamiltonian may be written [1]:

$$H_{\mathrm{s}1} = \sum_{i,j} S_i D_{ij} S_j \,, \; i, j = 1, 2, 3 \,.$$

The tensor D_{ij} is a linear function of the applied stress or strain, the constants of proportionality being the strain (G_{ijkl}) or stress (C_{ijkl}) spin-lattice coefficients:

$$D_{ij} = \sum_{kl} G_{ijkl} e_{kl} = \sum_{kl} C_{ijkl} X_{kl}$$

where X_{kl} and e_{kl} are the components of the external stress and induced strain tensors respectively. In cubic crystals there are only two independent strain spin-lattice coefficients, which are related to the stress spin-lattice coefficients through the host's elastic stiffness constants by the relationships:

$$C_{11} = C_{11}\,(c_{11} - c_{12}) \text{ and } G_{44} = C_{44} c_{44}$$

where we use the contracted notation for the suffixes.

The stress-induced shifts of the fine structure lines were measured at 77 K for the magnetic field lying along the directions [001], [$1\bar{1}0$] and [$1\bar{1}1$]. The spin lattice coefficients derived from these data and the elastic constants quoted in refs. [9] and [10] are given in table 1, together with those reported for Mn^{2+} in MgO [1] and CaO [2].

The linewidths of the Mn^{2+} transitions are temperature dependent and it is not possible to resolve the fine structure for temperatures higher than 100 K. The $1/2 \leftrightarrow -1/2$ lines showed an isotropic width independent of m_{I}, and its values measured at 1.5 K between peaks of the derivative were 7 gauss and 4 gauss for CdTe and ZnTe respectively. The $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ transitions were broader and anisotropic due to the built-in internal stress [1]. From the knowledge of the spin-lattice coefficients and the observed linewidth of the fine structure lines it is possible to make a quantitative estimate of the distribution of internal stress. For the analysis of the data ref. [1] was followed, assuming the observed linewidths to have two independent contributions ΔH_{i} and $\Delta H_{\mathrm{s}} \cdot \Delta H_{\mathrm{s}}$ is the contribution from random internal stress and ΔH_{i} the intrinsic linewidth which is taken to be independent of the electronic magnetic quantum number m_{s}. Uncorrelated probabilities $P(X_{ij})$ are assumed for the components X_{ij} of the internal stress tensor which are given by the Gaussian distributions:

$$P(X_{11}) = P(X_{22}) = P(X_{33}) = \sqrt{2/\pi\alpha}\, \exp(-2X_{11}^2/\alpha^2)$$

$$P(X_{12}) = P(X_{23}) = P(X_{13}) = \sqrt{2/\pi\beta}\, \exp(-2X_{12}^2/\beta^2)$$

The parameters α and β, root mean square values of the compression and shear stresses respectively characterize the internal stress state of the samples. From the data taken on unstrained samples we obtained the values for α and β which are given in table 2, where the values measured in MgO [1] CaO [11] are included for comparison. After cycling the samples up to 700 kg/cm of external stress, the linewidths of the $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ transitions were significantly increased thus supporting our assumptions about their origin. This increase was of 50% and 300% for ZnTe and CdTe respectively.

The intrinsic linewidth in CdTe is mostly due to the superhyperfine interaction of the Mn^{2+} ions with its Cd neighbours. A spread of lines with a 4.8 gauss wide Gaussian envelope was expected [6], but this structure was completely smeared out in our samples by dipolar broadening. In ZnTe the superhyperfine structure contributes only ~1 gauss [12] to the intrinsic linewidth.

Table 2
Internal stress parameters (in kg/cm^2)

	CdTe	ZnTe	MgO [1]	CaO [11]
α	47	62	104	665
β	38	81	96	151

Important progress has already been made towards the understanding of the processes which contribute to the ground state splitting in S-state ions [13]. The II-VI compounds have highly covalent bonds and for this reason we believe that the values of the spin-lattice coefficients here reported may offer a good test of the relative importance of the electrostatic, overlap and covalent mechanisms discussed in ref. [13]. However we have not endeavoured to make detailed calculations because the crystal field parameters Dq are not known in these systems. Any estimate of the ground state eigenfunction would then be based on ab-initio calculations of the crystal fields thus leaving considerable room for error.

References

[1] E. Feher, Phys. Rev. 136 (1964) A 145.
[2] R. Calvo, Z. Stroubek, R.S. Rubins and P. Zimmermann, Physics Letters 27A (1968) 143.
[3] R. Calvo, R. Isaacson and Z. Sroubek, Phys. Rev. 177 (1969) 484.
[4] S.B. Oseroff and R. Calvo, J. Phys. Chem. Solids 33 (1972) 2275.
[5] C. Fainstein and S.B. Oseroff, Rev. Scient. Instrum. 42 (1971) 547.
[6] J. Lambe and C. Kikuchi, Phys. Rev. 119 (1960) 1256.
[7] K. Falkowski, Acta Physica Polonica 22 (1967) 831.
[8] I. Chen, C. Kikuchi and H. Watanabe, J. Chem. Physics 42 (1965) 189.
[9] D. Belincourt, H. Jaffe and L.R. Shiozawa, Phys. Rev. 129 (1963) 1009.
[10] B.H. Lee, J. Appl. Physics 41 (1970) 2984.
[11] R. Calvo, M.C.G. Passeggi and C. Fainstein, Physics Letters 37A (1971) 201.
[12] T.L. Estle and W.C. Holton. Phys. Rev. 150 (1966) 159.
[13] R.R. Sharma, T.P. Das and R. Orbach, Phys. Rev. 149 (1966) 257; Phys. Rev. 155 (1967) 338; Phys. Rev. 171 (1968) 378.