

Electron Paramagnetic Resonance Detection of Lattice Distortion in Mn⁺⁺-Doped II-VI Compounds

REUBEN S. TITLE

*Thomas J. Watson Research Center, International Business Machines Corporation,
Yorktown Heights, New York*

(Received 10 May 1963)

Kikuchi and Azarbayejani explained the differences in the crystalline field parameter a and the hyperfine parameter A for Mn⁺⁺-doped ZnTe and CdTe on the basis of a model which assumed lattice distortions caused by the different ionic radii of Zn⁺⁺, Mn⁺⁺, and Cd⁺⁺. Measurements are reported for Mn-doped ZnSe and CdSe which are in agreement with the model. A comparison of the paramagnetic data for Mn⁺⁺ in the zinc and cadmium compounds of tellurium, selenium, and sulfur gives additional confirmation of the model.

IN a recent paper¹ Kikuchi and Azarbayejani pointed out that the cubic crystalline field parameter a was larger for Mn⁺⁺ in ZnTe than in CdTe, whereas the hyperfine structure parameter A was smaller in ZnTe. To explain this, they proposed a model noting that the ionic radius of the Mn⁺⁺ ion was intermediate in size between the ionic radii of Zn⁺⁺ and Cd⁺⁺. A substitution of Mn⁺⁺ for Zn⁺⁺ in ZnTe, therefore, requires a local expansion of the lattice to accommodate the Mn⁺⁺ ion, whereas a substitution of Mn⁺⁺ for Cd⁺⁺ in CdTe would require the lattice to undergo a local contraction.

The effect of such lattice distortions on the resonance parameters may be predicted from the measurements of Walsh² who observed that in MgO and ZnS, an increase of pressure on the crystal caused the parameter a for Mn⁺⁺ to increase and the hyperfine structure parameter A to decrease. From these results one would, therefore, expect that Mn⁺⁺ in ZnTe would have a larger field parameter a and a smaller hyperfine parameter A than Mn⁺⁺ in CdTe. This is what was observed.¹ The above effect on the resonance parameters may also be derived from a slightly different point of view. Because of the relative size of the Mn⁺⁺ ion compared to Zn⁺⁺ and Cd⁺⁺, there is a greater overlap of the electronic charge of the Mn⁺⁺ ion with that of neighboring anions in the zinc compound than in the cadmium compound. That is to say that the bonds in the Mn⁺⁺-doped zinc compound are more covalent than in the cadmium compound. The effect of an increase in covalency is to increase the parameter a and to decrease A ³ which is the same prediction as above. As a further check of the model postulating lattice distortions it was suggested¹ that measurements in Mn⁺⁺-doped zinc and cadmium compounds involving anions other than tellurium would be useful.

In this paper the paramagnetic resonance data for Mn⁺⁺ in ZnSe and CdSe are reported. The results are in agreement with the model of Kikuchi and Azarbayejani. In addition, as will be shown below, a comparison of the data for Mn⁺⁺ in the zinc and cadmium compounds

of tellurium, selenium, and sulfur gives additional confirmation of the model.

The data for the selenides are incorporated with the data for the tellurides and sulfides in Table I.⁴

In the case of CdSe and CdS only the data for Mn⁺⁺ in the hexagonal forms of the crystals are known. However, in ZnS, where the parameter a has been determined both in the cubic and hexagonal modifications,⁵ the values in the two forms were within a few percent of one another. For CdS only ($a-F$) is known. However, F is probably quite small and little error is involved in taking $a = (a-F)$.

It will be noticed from the table that in the case of each anion, tellurium, selenium, or sulfur, the data are in agreement with the model of Kikuchi and Azarbayejani, that is, the field parameter a is larger in the zinc compound than in the cadmium compound and the hyperfine parameter A is smaller in the zinc compound.

It will also be noticed in Table I that the relative size of the zinc compound lattice to that of the cadmium compound is the same for the three anions, Te, Se, and S (equal to about 0.94). On the basis of a point charge model the ratios of the crystalline field parameters a in the zinc and cadmium compounds should have therefore been the same for all three anions. However, it can be seen from the table that this ratio increases as the anion is changed from Te to Se to S from 1.06 to 1.38 to 2.04.

This result is easily understood as a consequence of the lattice distortion model of Kikuchi and Azarbayejani. Lattice distortion introduced because of the relative size of Mn⁺⁺ compared to Zn⁺⁺ and Cd⁺⁺ would be expected to be largest in the smallest size lattice, that is, in the sulfide. The distortion would be smallest in the largest lattice the telluride, which is what is observed.

It is also interesting to note in Table I that for each anion, Te, Se, or S the g value for Mn⁺⁺ in the zinc compound is larger than the g value for Mn⁺⁺ in the cadmium compound. It has been shown by Fidone and

¹ C. Kikuchi and G. H. Azarbayejani, *J. Phys. Soc. Japan* **17**, B-I, 453 (1962).

² Walter M. Walsh, Jr., *Phys. Rev.* **122**, 762 (1961).

³ R. S. Title, *Phys. Rev.* **130**, 17 (1963).

⁴ H. H. Woodbury and G. W. Ludwig, *Bull. Am. Phys. Soc.* **6**, 118 (1961).

⁵ J. Schneider (to be published).

TABLE I. The paramagnetic resonance data for the zinc and cadmium compounds of tellurium, selenium, and sulfur.

Crystal	Symmetry	Lattice dimensions (Å)	$T^\circ\text{K}$	g	A (10^{-4} cm^{-1})	a (10^{-4} cm^{-1})	D (10^{-4} cm^{-1})	F (10^{-4} cm^{-1})	Ref.
ZnTe	T_d^2	$a_0=6.07$	4.2	2.0105	-56.5	29.6			1, 4
CdTe	T_d^2	$a_0=6.49$ Ratio=0.936	4.2	2.0069	-57.5	27.7			1, 4
ZnSe	T_d^2	$a_0=5.67$	77	2.0055 ± 0.0005	-61.7 ± 0.1	19.7 ± 0.4			This paper
CdSe	C_{6v}^4	$a=4.299$ $c=7.010$ $a_0=6.06$ Ratio=0.935	77	2.0041 ± 0.0005	-62.2 ± 0.1	14.3 ± 1.0	15.6 ± 0.1	-2.0 ± 1.0	3, 5
ZnS	T_d^2	$a_0=5.43$	77	2.0022	-64.5 ± 0.1	7.94 ± 0.05			5
CdS	C_{6v}^4	$a=4.14$ $c=6.72$ ($a_0=5.85$) Ratio=0.930	77	2.0020	-66.0 ± 0.1	3.9 ± 0.1	8.2 ± 0.1		5

Stevens⁶ that there is a small positive contribution to the g value due to the overlap of the Mn^{++} wave function with the wave functions of the charges on the neighboring anions.

The model assuming lattice distortion caused by introducing Mn^{++} would predict more overlap of the Mn^{++} wave function with the wave functions of neighboring anions in the zinc compound than that in the cadmium compound. Therefore, a higher g value is expected in the zinc compound and is observed. (The results for the selenides and sulfides must, however, be carefully considered since data for CdSe and CdS were taken with hexagonal crystals.)

In summary, it is seen that the relative values of g ,

a , and A for Mn^{++} in zinc and cadmium compounds of the same anion can be understood on the basis of a model which assumes lattice distortions caused by the different ionic radii of Zn^{++} , Mn^{++} , and Cd^{++} . The changes in the resonance parameters in going from one anion to the next (from Te to Se to S) as distinct from comparing zinc and cadmium compounds of the same anion are due to changes in the covalent character of the bonds for the different anions as has previously been pointed out.^{1,3,7}

I wish to thank J. A. Kucza for growing the Mn^{++} -doped ZnSe and CdSe and E. E. Tynan for aid in taking the paramagnetic data.

⁶ I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **A73**, 116 (1959).

⁷ J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955); O. Matsumura, J. Phys. Soc. Japan **14**, 108 (1949); T. P. P. Hall, W. Hayes, and F. I. B. Williams, Proc. Phys. Soc. (London) **A78**, 883 (1961).