purity ion itself causes a local structure distortion, is not known. It is interesting to note however, that if the latter were the case, then an interpretation would be required which would predict essentially the same mosaic angle for ions having widely varying ionic radii and for divalent as well as trivalent ions. Work along these lines is currently in progress at this laboratory.

In conclusion, the authors would like to express their indebtedness to Mr. Alfred Attard for his x-ray diffraction analysis.

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DISCUSSION

W. Low: Dr. D. Shaltiel and I have measured the anisotropy in the line width of gadolinium in thorium oxide. We have analysed these data along the lines of Dr. Marshall and in the particular crystal we found a deviation of 0.17° using a Gaussian distribution.

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Spin Resonance Properties of ZnTe:Mn and of Other $A_{II}B_{VI}$ Compounds

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The cubic field splittings $3a$ for ZnTe:Mn and CdSe:Mn are reported. The ground state splittings in ZnTe and CdTe, whose lattice parameters are 6.10 and 6.48Å, are 88.9 and 83.1×10^{-4} cm^{-1}, respectively. On the other hand, for CdSe, for which the lattice parameter is 6.05Å, the cubic field splitting is 46.3×10^{-4} cm^{-1}. It is suggested that the impurity Mn^{++} ions produce local dilatations such as to be under compression in the zinc $A_{II}B_{VI}$ compounds and under tension in the corresponding cadmium compounds.

These investigations were motivated by the results of measurements of the Mn^{++} ions in the $A_{II}B_{VI}$ compounds reported earlier.[1)2)] Baker, Bleaney, and Hayes[3)] noted that the cubic field splitting $3a$ for ZnS:Mn is in contradiction to Watanabe's theory[4)], whereas the results for Mn^{++} in MgO and CaF_2 appeared to be consistent with the theoretical predictions. Subsequent measurement of $3a$ for CdTe:Mn showed that the experimental results cannot be reconciled with Watanabe's theory, or with the more refined calculations by Powell, Gabriel, and Johnson[5)]. In this paper, we report the results for ZnTe:Mn and CdSe:Mn.

The surprising result is that $3a$ for Mn^{++} ions in both ZnTe and CdTe are very nearly equal, as are the hfs coupling constants A, despite the marked difference in the lattice parameters. On the other hand, the lattice parameters for CdSe and ZnTe are very nearly equal; yet the cubic field splitting $3a$ for CdSe is almost one half of that of ZnTe. As a tentative explanation of these observed results, we propose that the impurity Mn^{++} ions produce local distortions so as to produce the nearest neighbor environment that is almost independent of the host crystal.

The experimental procedures used in the determination of the spin Hamiltonian parameters for ZnTe:Mn were identical to those used for CdTe:Mn reported earlier[2]. The Mn^{++} spectrum can be observed at room temperature, but the bulk of the measurements was made at 78° and 4.2°K. The *g*-value at 78°K is about 2.005. The cubic field splittings at 78° and 4.2°K. are about 89.1 and $88.9\times10^{-4}\,cm^{-1}$ respectively. The hfs coupling constant is about 56.3×10^{-4} cm^{-1}. The temperature dependence of *A* of Mn^{++} in ZnS, ZnTe, and CdTe were measured. In all cases, there appears to be a progressive increase in *A* as the temperature is lowered.

Single crystals of ZnTe:Mn were prepared for us by Professor D. Mason, of the Chemical and Metallurgical Engineering Department. Stoichiometric amounts of Zn, Mn, and Te were weighed into a clear fused silica tubing and sealed at pressures below 10^{-4} mm of Hg. The sample was heated to 1350°C for about seven minutes, and subsequently annealed at 1000°C for about two weeks.

The following table (Table I) is intended to facilitate comparison of Mn^{++} in Zn and Cd $A_{II}B_{VI}$ compounds.

Table I. Hyperfine Structure and cubic field splittings.

	S			Se			Te		
	a_0	A	$3a$	a_0	A	$3a$	a_0	A	$3a$
Zn	5.43	63.8	23.3	5.67	60	—	6.10	56.5	88.9
Cd	5.85	64.8	—	6.05	61.5	46.3	6.48	57.5	83.1

a_0 in Angstrom units; A, $3a$ in units of $10^{-4}\,cm^{-1}$.

Some of the hfs constants in the above table are taken from the paper by Matsumura[8]. The results quoted for ZnTe and CdTe are for 4.2°K. We note that the *A's* are determined primarily by the coordination anions; however, it is interesting to note that the hfs coupling constants of Mn^{++} in the zinc compounds are consistently smaller than in the corresponding cadmium compounds. The results for ZnTe and CdTe suggest that *3a* may also depend principally upon the nearest neighbor anions.

A possible explanation of the experimental results is that Mn^{++} ions introduced into an otherwise pure crystal will produce local distortions. The ionic radii of Zn^{++}, Mn^{++}, and Cd^{++} are 0.83, 0.91, and 1.03Å, respectively. A reasonable assumption is that the effective radii in the $A_{II}B_{VI}$ compounds are also in the order Zn^{++}, Mn^{++}, and Cd^{++}. Consequently, the lattice needs to undergo local expansion to accommodate a Mn^{++} ion in the zinc compound, whereas local contraction will take place in the immediate vicinity of Mn^{++} ions in the corresponding cadmium compound. Therefore, the Mn^{++}-anion distance in the zinc compound can be expected to be somewhat smaller than in the cadmium compound. Such a hypothesis can qualitatively account for the small differences in *A* and *3a*, since recently Walsh[9] has shown that *A* decreases and *3a* increases with increasing pressure. A crucial test of these conjectures can be provided by ZnSe:Mn.

Additional evidence for distortions produced by impurities is provided by Ogawa[10], who investigated the superhyperfine structure of fluorine due to Mn^{++} ions in the compounds $KMgF_3$, $KCdF_3$, and $KCaF_3$, which have the cubic perovskite structures. The results are presented in Table II.

Table II. $Mn^{++}-F^-$ distances from superhyperfine structure.

KMF_3	M^{++}-F^- dist. (X-ray)	Mn^{++}-F^- dist. (calc.)	A ($10^{-4}\,cm^{-1}$)
$KMgF_3$	1.994 A	2.080 A	91.2
$KCdF_3$	2.167	2.119	92.6
$KCaF_3$	2.187	2.124	93.1
$KMnF_3$	2.095	2.095	

The numbers in the second column indicate the divalent metal-fluorine distance as measured by x-rays. We note that the hfs constant increases with increasing M^{++}-F^- distance. The numbers in the third column indicate the calculated Mn^{++}-F^- distances in the otherwise pure KMF_3 crystals from the superhyperfine structure of fluorines surrounding the Mn^{++} ions. If these calculated results are compared with the Mn^{++}-F^- distance in $KMnF_3$ determined by x-rays[11], we note that the Mn^{++} ions are under compression in $KMgF_3$ and under tension in $KCdF_3$ and $KCaF_3$.

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DISCUSSION

W. Low: I should like to comment briefly on the variation of the initial splitting of the ^6S ground state. Gabriel *et al.* have diagonalized the matrix of the cubic field with spin-orbit coupling using a convergent perturbation technique. M. Rosengarten and W. Low have diagonalized the complete matrix of the cubic field and spin-orbit coupling. While our results differ numerically both results show that the initial splitting and the optical spectra can be fitted simultaneously by having an enlarged spin-orbit coupling compared with the free ion value. This result is not yet understood. However variations in *3a* can be understood in the main by changing the spin-orbit coupling parameter. The changes in the Slater integral and possibly in the spin-orbit coupling may be correlated with covalency effects.

C. Kikuchi: The discrepancies that you mention might arise because of the ionic approximation. I have not been convinced that such an approximation is applicable when the band gap of the host crystal is comparable to or smaller than the distance to the excited states of the free Mn^{++} ions.

B. Bleaney: Presumably the abnormally large values of cubic field splitting in these compounds are associated with a considerable degree of covalent bonding; the latter is indicated by the unusually small values of the Mn^{55} hyperfine structure, which have normally been ascribed to the effects of covalent bonding.

C. Kikuchi: I agree with you. However, here, we are concerned with local distortions in pairs of related compounds, such as CdTe and ZnTe, and not with such a pair as CdSe and CdTe.