with respect to it. A typical series of semiconductors arranged in order of increasing ΔP is the so-called isoelectronic[2] series of Ge, namely, Ge, GaAs, ZnSe, and CuBr. The isoelectronic series of Si and Sn can be written down on examining a periodical table. Making these assumptions, we conclude:

(a) The first two bands move apart and the band gap increases with increasing the charge difference, $2\Delta P$, and also as α decreases from the symmetrical case of $\alpha = \frac{1}{2}$ towards zero.

(b) The effective mass increases monotonically with ΔP which measures the ionic component in the binding of the crystal.

The first result agrees qualitatively with experience.

Not enough experimental evidence is available to compare the second result with experience. However, it does correct the previously published conclusion of Seraphin based also on the same model.

Sign of the Crystalline Cubic Field Splitting Parameter a in an S State*

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(Received July 18, 1956)

Measurements of the paramagnetic resonance spectrum of manganese and ferric ions at low temperatures yield the values for the cubic field splitting parameter a as 18.6×10^{-4} and 205×10^{-4} cm^{-1} respectively. The sign of a is positive in both cases, indicating that the twofold degenerate level is lower than the fourfold degenerate level. This is in contrast with Bleaney and Trenam's results on ferric alums who find a negative a. For gadolinium in CaF$_2$, the constant $a = 175 \times 10^{-4}$ cm^{-1} and is also positive.

THE ion Mn^{2+} and the isoelectronic Fe^{3+} have a ground state of $^6S_{5/2}$. Bethe[1] has shown that a cubic field splits the sixfold degeneracy of the free ion into a twofold and fourfold degenerate level. Van Vleck and Penney[2] have discussed the mechanism by which such a splitting can be effected, and have shown that the crystalline cubic field can influence the electron spins only through higher order interactions involving spin-orbit coupling with excited states. These considerations give, however, no indications whether the twofold or the fourfold level lies lower. It is moreover of interest to determine the level scheme in a pure cubic field experimentally.

We have determined the sign of a, the cubic field splitting parameter, for Mn^{2+} and Fe^{3+} in cubic fields as follows. The transitions of the five fine-structure lines for very strong magnetic fields are given to the first order by

$$M = 1/2 \rightarrow -1/2, \quad H = H_0;$$
$$M = \pm 3/2 \rightarrow \pm 1/2, \quad H = H_0 \pm (5/2)pa;$$
$$M = \pm 5/2 \rightarrow \pm 3/2, \quad H = H_0 \mp 2pa;$$

where $3a$ is the splitting between the twofold and fourfold level, $p = 1 - 5\phi$, $\phi = l^2m^2 + l^2n^2 + m^2n^2$ and l, m, n, are the direction cosines of the magnetic field with respect to the cubic axes of the crystal. Therefore, if a be positive, then for the [100] direction ($\phi = 0$) the $-5/2 \rightarrow -3/2$ transition should fall at magnetic fields higher than H_0 and the transition $-3/2 \rightarrow -1/2$ at fields lower than H_0. By observing the relative intensities of the fine-structure lines at liquid helium temperature, one can assign the correct quantum numbers to the various transitions. We find that for Mn^{2+} and also for Fe^{3+} in the cubic field of MgO (octahedral NaCl structure), the $-3/2 \rightarrow -1/2$ transition falls at a lower and the $-5/2 \rightarrow -3/2$ transition at a higher field than the central $1/2 \rightarrow -1/2$ transition. This corresponds to a positive a. In ZnS (cubic, tetrahedral symmetry) one finds that a is negative for Mn^{2+}. The results are summarized for various crystals in Table I.

At first glance this might suggest that the sign of a is determined by the sign of D in the cubic crystalline potential $V = D(x^4 + y^4 + z^4 - \frac{3}{5}r^4)$. In an octahedral arrangement D and a are positive, and in a tetrahedral arrangement D and correspondingly a are negative. Bleaney and Trenam's results[3] of a negative a in ferric alums cast considerable doubt on such an explanation. The

[1] H. Bethe, Ann. Physik 3, 133 (1929).

[2] J. H. Van Vleck and W. G. Penney, Phil. Mag. 17, 961 (1934).

[3] B. Bleaney and S. Trenam, Proc. Roy. Soc. (London) A223, 1 (1954).

TABLE I. Magnitude and sign of a for Mn^{2+}, Fe^{3+}, and Gd^{3+} in various crystals.

Ion	Crystal	Cubic field symmetry	a in cm^{-1}	g	Reference
Mn^{2+}	$(NH_4)_2Zn(SO_4)\cdot 6H_2O$	Appr. octahedral	$+0.0005$	2.000 ± 5	a
	$ZnSiF_6 \cdot 6H_2O$	Appr. octahedral	$+0.0007$	2.000 ± 5	a
	$Mg_3Bi_2(NO_3)_{12} \cdot 24H_2O$	Appr. octahedral	$+0.0010$	1.997 ± 3	b
	MgO	Octahedral	$+0.00186$	2.0014 ± 5	This paper
	ZnS	Tetrahedral	-0.00076	2.000	c
Fe^{3+}	$KAl(SeO_4)\cdot 12H_2O$	Appr. octahedral	-0.0127	2.003 ± 3	d
	MgO	Octahedral	$+0.0205$	2.0037 ± 7	This paper and e
Gd^{3+}	CaF_2	Fluorite	$+0.0175$	1.991 ± 1	This paper

a B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).
b R. S. Trenam, Proc. Phys. Soc. (London) **A66**, 118 (1953).
c L. M. Matarrese and C. Kikuchi, Phys. Rev. **100**, 1243 (A) (1955). (These authors have determined the sign of a in ZnS from hyperfine considerations.)
d B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).
e W. Low, Bull. Am. Phys. Soc. Ser. II, **1**, 283 (1956). The cubic field splitting was erroneously reported there as $|3a| = 548$. It should read 658 gauss.

structure of α ferric alum shows that each trivalent ion is surrounded by a nearly regular octahedron of six water molecules and the sign of a would be expected to be positive. Moreover, preliminary results[4] indicate that the sign of a in Gd^{3+} in the cubic field of CaF_2 (fluorite structure, D negative) is positive.

These differences in the sign of a for the various crystals, as well as the variations in the g factor—the g factor of Fe^{3+} being larger than g_e (that of the free electron) while the g factor of Mn^{2+} and Gd^{3+} is less—are at present puzzling. It is probable that a solution of this problem will depend on an accurate calculation of the various excited states (^4P, ^4D, ^4G, etc.). It is possible that departures from cubic symmetry like in the alums might change the order of some of the energy levels.

The author gratefully acknowledges friendly encouragement from Professor C. A. Hutchison, Jr.

4 W. Low (to be published).

Paramagnetic Resonance Spectrum of Manganese in Cubic MgO and CaF2†

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(Received August 21, 1956)

The paramagnetic resonance spectrum of manganese in cubic MgO and CaF_2 has been analyzed at wavelengths of one and three cm. The cubic field splitting in MgO is given by $3a = (+55.9 \pm 0.9) \times 10^{-4}$ cm^{-1}. The twofold degenerate level lies lower than the fourfold degenerate level. The hyperfine structure constant is $A = (-81.0 \pm 0.2) \times 10^{-4}$ cm^{-1}; $g = 2.0014 \pm 0.0005$. The large cubic field splitting and the reduced hyperfine structure point towards considerable covalent bonding. Anomalous intensity ratios of the fine structure lines were observed. In CaF_2 the hyperfine structure constant has a value of $A = (95 \pm 1) \times 10^{-4}$ cm^{-1}. The line width of 40 gauss even at very low concentration prevented any resolution of fine structure. The large line width is probably caused by the interaction of the magnetic electrons with the fluorine ions.

INTRODUCTION

THE paramagnetic resonance spectrum of manganese has a number of unusual and interesting features. Divalent manganese has five $3d$ electrons, a half-filled electron shell. The resultant angular momentum is therefore zero and the paramagnetism arises only from the electronic spins. Bethe[1] has shown from group theoretical reasoning that a cubic field removes the sixfold degeneracy of the $^6S_{5/2}$ ground state and splits it into a twofold and fourfold degenerate level. The mechanism responsible for this splitting is imperfectly understood. Van Vleck and Penney[2] have suggested that the splitting arises from the action of both the cubic field and spin-orbit interaction; each mechanism separately is unable to give any splitting to any order of approximation. The splitting of the S state can be viewed as being due to admixtures from higher states of the $3d^5$ configuration to the ground state. These higher excited states are in turn split by

1 H. Bethe, Ann. Physik **3**, 133 (1929).
2 J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).