

A detailed article will be published shortly in *Applied Science Research*.

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¹ H. Faxén and J. Holtmark, *Z. Physik* **45**, 307 (1927); see N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, chap. II.

² J. Friedel, *Phil. Mag.* **43**, 153 (1952), form. 2, p. 157.

³ D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A157**, 490 (1936).

⁴ D. L. Dexter, *Phys. Rev.* **87**, 768 (1952).

Paramagnetic Resonance in Manganese Formate

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THE paramagnetic resonance spectra of two salts of manganese have been studied in detail by Bleaney and Ingram,¹ and an analysis of the five groups of six hyperfine structure lines made in terms of the electronic splitting and crystalline field symmetries. Measurements are reported here on the spectra obtained from crystals of diluted manganese formate, and are of interest in that the electronic splitting is considerably greater than usual, being twice that observed in any inorganic salt so far.

All the measurements were made at room temperature and at a wavelength of 1.25 cm, the magnetic field being calibrated by means of normal proton resonance methods, and a modulating sweep being used for detection and display. The crystals of $Zn(HCOO)_2 \cdot 2H_2O$ and $Mn(HCOO)_2 \cdot 2H_2O$ are both monoclinic prismatic with very nearly equal axial angle and ratio; $\beta = 97^\circ 19'$ and $97^\circ 38'$, respectively.² The paramagnetic absorption spectra show that there are two ions per unit cell, as in the case of the Tutton salts.¹

Rotation in the plane of crystallographic symmetry (i.e., xz plane), in which the spectra of the two ions coincide, showed that the electronic splitting remains small in all directions, indicating that the crystalline field axes of the two ions must lie near the y axis. A maximum occurs at an angle of $+7^\circ$ to the z axis, and, in order to establish whether this direction was K_1 or K_2 , the crystal was rotated in the two planes (a) through the y axis and $+7^\circ$ to z , and (b) through the y axis and $+97^\circ$ to z .

Rotation in the first plane gives an electronic splitting which has a maximum along the y axis, with a subsidiary one at right angles, and this shows that it is the K_2K_3 plane. Hence K_1 makes an angle of $+97^\circ$ to z in the xz plane.

Rotation in the second plane (K_1K_3) gives two maxima, corresponding to the largest electronic splittings obtained in the crystal, at angles $\alpha = \pm 62^\circ$ to K_1 . This explains why the separation along K_1 is small, as the electronic splitting goes through a minimum at about 60° to the crystalline field axis.

The separations between the centers of the five groups along the three crystal axes, and the axis of the crystalline field of the Mn^{++} ion, are listed in Table I.

The hyperfine structure separation remains constant with a splitting of 98 gauss between successive lines. In analyzing the spectra the usual Hamiltonian,

$$\mathcal{H} = g\beta H \cdot S + D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) + F(a) + AS_xI_x + B(S_xI_x + S_yI_y),$$

is used, and from the expressions^{3,4} for the separation between successive groups along the field axis, one obtains for the coefficients, in units of 10^{-4} cm^{-1} :

$$A = B = 91, \quad D = 485, \quad E = 110, \quad a = 9.5.$$

The accuracies are to within 1 percent for A , B , and D , but since evaluation of E depends on second-order effects its accuracy

TABLE I. Electronic splittings along different axes.

Direction	Separation of groups (gauss)			
x axis	280	290	285	280
y axis	860	630	650	475
z axis	355	420	480	480
Field axis	1105	1020	1010	1065

is much smaller. E can also be estimated from the splitting obtained along different directions at right angles to the field axis. These vary from 1060 gauss to 2950 gauss, measured between the extreme groups, and give 85 ± 40 as a probable value of E .

The g value was determined by means of a free-radical marker and, allowing for the second-order corrections, was evaluated as $g = 1.999 \pm 0.0015$.

It is of interest to compare these results with those obtained from other manganese results,^{1,3-5} as is shown in Table II.

TABLE II. Comparison of splittings in different salts. The coefficients are given in units of 10^{-4} cm^{-1} .

Salt	D	A	a	E	Reference
$Mn(COOH)_2 \cdot 2H_2O$	485	91	9.5	110	—
$Mn(CH_3COOH)_2 \cdot 4H_2O$	412	87	8	56	4
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	243	91	5	100	1
$Mn(NO_3)_2 \cdot 2Bi(NO_3)_3 \cdot 24H_2O$	180	90	10	—	5
	164	88	10	—	
$Mn(CH_3COOH)_2 \cdot 3H_2O$	252	—	—	27	3
$MnSiF_6 \cdot 6H_2O$	197	96	7	—	1

The first four salts all have two ions per unit cell, and it is seen that D decreases as the number of waters of crystallization increases; as is also the case for the last two, which have only one ion per unit cell.

This confirms the fact that the symmetry of the crystalline field round the paramagnetic ion is probably mainly due to the water molecules in all the salts investigated.

¹ B. Bleaney and D. J. E. Ingram, *Proc. Roy. Soc. (London)* **A205**, 336 (1951).

² P. Groth, *Chemische Kristallographie* (Leipzig, 1910), Vol. 3, p. 18.

³ Kumagai, Ono, Hoyahi, and Kambe, *Phys. Rev.* **87**, 374 (1952).

⁴ D. J. E. Ingram, *Proc. Phys. Soc. (London)* **A66**, 412 (1953).

⁵ R. S. Trenam, *Proc. Phys. Soc. (London)* **A66**, 118 (1953).

An Excitation Curve for Photomesons from Beryllium*

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THE yields of 54-Mev π^- and π^+ mesons at 90° were obtained as a function of the maximum energy of the Cornell synchrotron. A double-focusing magnet deflects the mesons through 90° into a proportional counter telescope. The solid angle and energy resolution of the magnet were determined by means of a current-carrying wire. The full width at half-maximum was 25 Mev. The angular aperture was $\pm 7^\circ$ horizontally and $\pm 3.5^\circ$ vertically. Agreement was found with the strong energy dependence of the π^-/π^+ ratio observed by Littauer and Walker at 135° .¹ The following ratios were obtained.

Maximum gamma-ray energy (Mev)	310	275	250	225
Ratio π^-/π^+	1.65 ± 0.05	2.0 ± 0.1	2.4 ± 0.3	3.3 ± 0.5

The maximum energy of the bremsstrahlen was varied by turning off the accelerating rf at the appropriate part of the magnetic cycle. The beam was monitored by an ionization chamber behind 1 inch of copper. The response of the chamber is nearly proportional to the total energy in the gamma-ray beam in the region from 200- to 300-Mev maximum energy.² By the subtraction of the yields normalized to the same number of "equivalent quanta"