

These add up to about 0.13 *atom* percent of total detected impurity.

A more extensive series of measurements was made on the polycrystal specimens. Hydrogen or nitrogen was condensed in the inner Dewar which was ordinarily used for helium. This Dewar was surrounded by a bath of nitrogen so that heat leak into the inner dewar was very small and the temperature stability was excellent. The temperatures of the samples were calculated from the observed vapor pressure of nitrogen or hydrogen. At room temperature and the ice point the temperature was measured with a copper-constantan thermocouple. The ratio of the resistance at various temperatures to that at the ice point is given in Table III. The precision of the resistance measurements was about 0.1 percent.

An anomalous behavior of the resistivity of the 30 percent thallium specimen was observed in the nitrogen range. This is shown in Fig. 1. The ordinate is the

thermal part of the specific resistance, $\rho(T) - \rho(0^\circ\text{K})$, for the 20, 30, 38, and 50 percent samples, less the corresponding quantity for the 15 percent sample, which was arbitrarily taken as a standard for comparison. Although because of possible errors in the dimensional measurements the specific resistance is known only to 1 or 2 percent, for a given sample its fractional variation with temperature is known much more accurately. The anomaly in the temperature variation of the 30 percent specimen occurring over the range 45–60°K is very likely an indication that in this temperature interval the specimen is changing from a high temperature face-centered cubic form to a low temperature face-centered tetragonal one. Such an assumption fits well an extrapolation of the composition-temperature curve for the cubic-tetragonal transformation found by Guttman.³

³ L. Guttman, J. Metals (Trans. Am. Inst. Mining Met. Engrs. **188**, 1472 (1950)).

Paramagnetic Resonance in Phosphors*

W. D. HERSHBERGER AND H. N. LEIFER
University of California, Los Angeles, California
(Received July 7, 1952)

Paramagnetic studies at 9375 Mc have been made on 32 inorganic phosphors containing paramagnetic activators. The sample is contained in a transmission cavity and the spectrum is obtained by a sweeping technique that yields the derivative of the absorption curve. Less than 10^{-11} mole of Mn^{++} may be detected in cubic host crystals. The specimen in the cavity may be illuminated by ultraviolet light for observations on changes in its spectrum under these conditions, but, when illuminated, the changes observed may be attributed largely to photoconduction. The phosphors containing Mn^{++} as an activator under no illumination yield a variety of spectra. Seven of these phosphors display a single absorption line 750 to 1000 gauss wide, while four phosphors with different host crystals but all having cubic symmetry display line spectra consisting of six lines seven gauss wide but with spacings between members of from 68 to 88 gauss depending on the host crystal. Finally, two phosphors display 30-line spectra which arise because the crystal field and the applied field together serve to remove both the *I* and *S* degeneracy, whereas for cubic crystals only the *I* degeneracy is removed.

INTRODUCTION

EXPERIMENTAL methods for observing paramagnetic resonance¹ at microwave frequencies provide means for obtaining precise and detailed information on the energy levels occupied by electrons in solids. In general, depending on the experimental technique employed, line spectra will be observed only when an adequate number of electrons with unpaired spins occur in a material and when the various factors which determine line width are favorable, such as, for example, the lifetime of the state under study or the magnitude and character of the interactions between ions and the crystal field. Such spectra should be par-

ticularly instructive when found in phosphors and other semiconductors. For example, in phosphors, the set of transitions involved in the processes of fluorescence and phosphorescence are at present imperfectly understood in any quantitative sense. Experiments on photoinduced changes in paramagnetism have been reported both for organic² and inorganic³ phosphors, but these experiments make use of bulk ponderomotive effects. In the present study, the paramagnetic spectra of a number of inorganic phosphors were taken at 9375 Mc requiring magnetic fields in the 3000–3500 gauss range. The emphasis has been placed on phosphors in which small proportions of doubly ionized manganese (Mn^{++}) are used as activators in a variety of host crystals. Mn^{++} is

* Work supported in part by the ONR.

¹ E. Zavoisky, J. Phys. (U.S.S.R.) **9**, 211, 245, 447 (1945); **10**, 170, 197 (1946); R. L. Cummerow and D. Halliday, Phys. Rev. **70**, 443 (1946); D. M. S. Bagguley and J. H. E. Griffiths, Nature **160**, 532 (1947).

² G. N. Lewis and M. Calvin, J. Am. Chem. Soc. **67**, 1232 (1945).

³ P. D. Johnson and F. E. Williams, J. Chem. Phys. **17**, 435 (1949).

in an S -state, its $3d$ -shell consists of five unpaired electrons, and as a result of low spin-orbit coupling we may expect long relaxation times and relatively narrow line spectra. The changes observed in the phosphors under irradiation may at present be attributed largely to photoconduction, but changes in paramagnetism under irradiation should exist and be observable if conditions favorable for the excitation of a sufficient number of luminescent centers can be met.

The spectra of unirradiated phosphors are sufficiently interesting and varied to warrant a separate treatment. In the present paper, the experimental method in use is described, and results on the spectra of some thirty unirradiated phosphors are reported together with a discussion of their most interesting features.

EXPERIMENTAL METHOD

Observations on the phosphors are carried on at a fixed frequency of approximately 9375 Mc. The sample itself often was in the form of a wafer, perhaps $\frac{1}{8}$ inch in diameter and $\frac{1}{32}$ inch thick and was placed to intersect the axis of a resonant cavity operating in the circular electric or TE_{011} mode. Again, a thin layer of phosphor was placed in a shallow cup in the cavity. The TE_{011} mode was chosen, in part, because it is the low-loss or high Q mode, and in part, because an aperture for sample illumination may readily be cut in the end of the cavity without appreciably disturbing the field. The loaded Q of the cavity with the sample in position was of the order of 10,000. Further, in this mode, the rf magnetic field is concentrated along the axis of the cavity yielding high sensitivity with a small sample and at the same time the condition for resonance—rf field perpendicular to the external magnetic field—may readily be satisfied. The magnet has 8-inch diameter pole pieces, and a $2\frac{1}{2}$ -inch gap was used so the effect of field inhomogeneity on line width is negligible.

In searching for paramagnetic spectra, the magnetic field is swept over a 500-gauss range in perhaps 4 minutes and is simultaneously swept 2 to 5 gauss at a 40-cycle rate. The low speed wide range sweep is accomplished by varying the set point on an electronically regulated supply furnishing power for the main magnet coils, while separate low inductance coils are employed for injecting the low amplitude 40-cycle sweep. The band width of the detection system is approximately 3 cycles. As a result of the method employed in collecting information from the sample, the derivative of the paramagnetic absorption curve or curves is obtained. Changes in power transmitted through the cavity containing the sample are detected and recorded using either a square law detector or a phase detector following a 40-cycle amplifier. Signal to noise ratios in excess of 1000 are obtained with a 10-mg sample of cubic zinc sulfide activated with manganese present to 1 part in 10^5 , indicating that less than 10^{-11} mole of manganese may be detected.

Magnetic field strength is measured by comparing the frequencies of two equipments used simultaneously in the same magnet. The cavity of one equipment contains the phosphor under study, while the second cavity, operating at a different frequency, contains a small quantity of diphenyl-trinitrophenyl-hydrazyl.⁴ Since the g -value of the hydrazyl is given as 2.0036 ± 0.0002 and is quite accurately known,⁵ a frequency comparison is sufficient to determine the positions of the peaks of the paramagnetic spectrum of the phosphor. Field strength is measured with an accuracy of ± 1 gauss.

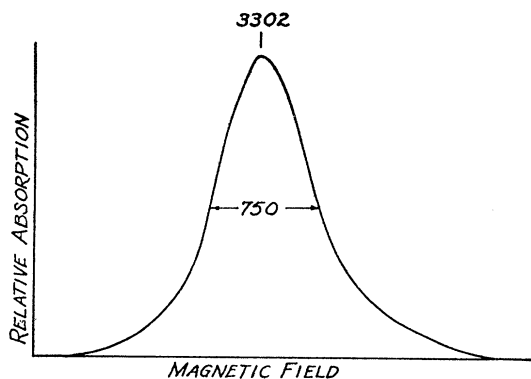
In taking the spectra of irradiated samples, sources rich in either 2537A or 3640A were used depending on the characteristics of the phosphor under study. In one procedure, steady illumination is used and both the slow wide range magnetic sweep and the 40-cycle sweep are used. The original spectrum characteristic of an unilluminated sample is found—masked somewhat by photoconduction in some instances—and a search is made for a new spectrum which could perhaps arise from trapped electrons or a modified manganese ground state. The failure to detect such spectra may mean only that trapping or other changes occur to an insufficient degree in the phosphors studied in view of the detection sensitivity now available, or that the spectra are too broad to be observed readily. In a second procedure, only the slow wide range sweep is employed, but intermittent 40-cycle illumination is used on the phosphor in an attempt to detect differences between spectra characteristic of an illuminated and an unilluminated phosphor sample. The only conclusion one can reach from the negative result for a phosphor in which a signal to noise ratio of 100 is observed for the unilluminated sample, is that less than 1 percent of the contributing manganese ions experience changes in their paramagnetic properties on illumination, or that in some instances, changes in paramagnetism may be masked by changes in conductivity produced by the illumination. These latter changes of course occur at all values of the magnetic field, including zero.

The changes in dielectric constant in phosphors on illumination which have been reported,⁶ probably have little effect on microwave transmission, since the relaxation time associated with these changes is of the order of 10^{-7} second, which is long compared with the period of the microwaves. In the transmission experiments reported here, susceptibility changes cannot be differentiated from changes in conductance as in more complicated experimental procedures. However, these latter methods would be particularly valuable when photoconduction masks the permeability changes sought.

⁴ Furnished by A. N. Holden of Bell Telephone Laboratories.

⁵ A. N. Holden *et al.*, Phys. Rev. **77**, 147 (1950).

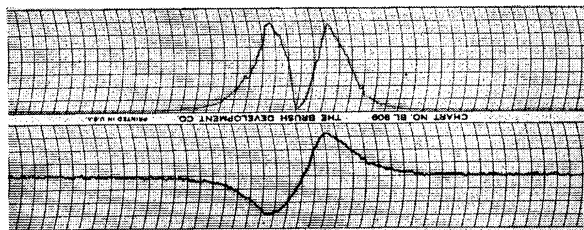
⁶ G. F. J. Garlick, *Luminescent Materials* (Oxford Press, London, 1949), Chapter V.

FIG. 1. Absorption of tetr. $\text{ZnF}_2:\text{Mn}$ (0.04).

EXPERIMENTAL RESULTS

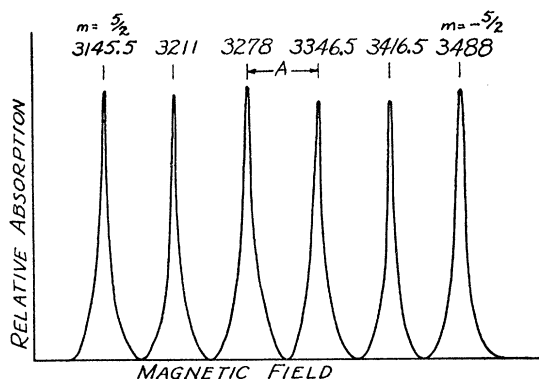
The phosphors investigated have been classified into five groups according to their observed spectra. The first four groups contain all the manganese activated phosphors; the fifth group contains all others.⁷

The members of group one are: tetr. $\text{ZnF}_2:\text{Mn}$ (0.04); rbhdl. $\text{Zn}_2\text{SiO}_4:\text{Mn}$ (16); rbhdl. $8\text{ZnO}\cdot\text{BeO}\cdot 5\text{SiO}_2:\text{Mn}$ (0.25); rbhdl. $\text{Zn}_2\text{GeO}_4:\text{Mn}$ (0.01); rbhdl. $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}$ (0.05); rhomb. $\text{CdSiO}_3:\text{Mn}$ (0.018); rhomb.

FIG. 2. Experimental record tetr. $\text{ZnF}_2:\text{Mn}$ (0.04).

$\text{Mg}_2\text{GeO}_4:\text{Mn}$ (0.01). The spectrum of each member of this group is a single broad absorption curve, 750–1000 gauss wide, as typified in Fig. 1. This curve was constructed using data from Fig. 2 which is an experimental record taken with tetr. $\text{ZnF}_2:\text{Mn}$ (0.04) as the phosphor.

The members of group two are: cubic $\text{ZnS}:\text{Mn}$ (0.001); cubic $\text{ZnAl}_2\text{O}_4:\text{Mn}$ (0.001); $\text{MgO}:\text{Mn}$ (0.1 mole percent) [197-2]; $\text{MgO}:\text{Mn}$ (0.1 mole percent) [200-2]. Each member of group two displays a six-

FIG. 4. Absorption of cub. $\text{ZnS}:\text{Mn}$ (0.001).

peaked hyperfine spectrum as typified in Figs. 3 and 4. Of interest is the very large (A'' gauss) and isotropic hyperfine spectrum for S state Mn^{++} . It should also be noted that the hyperfine splitting, A , differs for each material as shown in Table I. Finally, the absorption signal for $\text{MgO}:\text{Mn}$ [200-2] is 10 percent, in magnitude, of $\text{MgO}:\text{Mn}$ [197-2], both having the same manganese concentration.

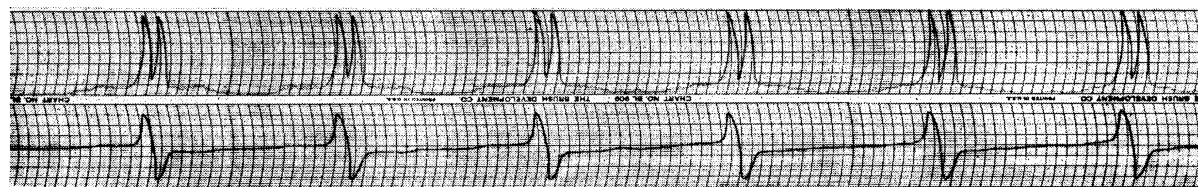
There are two members in group three: hex. $\text{ZnS}:\text{Mn}$ (0.01) and $\text{ZnS}:\text{Tb}$ (0.04): Mn (0.005). The 30-peak spectrum of these two phosphors is a superposition of fine and hyperfine splitting shown in Figs. 5 and 6.

The members of group four are: rbhdl. $\text{Zn}_2\text{SiO}_4:\text{Mn}$ (0.25); rbhdl. $\text{Zn}_2\text{SiO}_4:\text{Mn}$ (1); rhomb. $\text{CdSO}_4:\text{Mn}$ (0.006); rhomb. $\text{ZnSO}_4:\text{Mn}$ (0.006); $\text{ZnO}\cdot\text{B}_2\text{O}_3:\text{Mn}$ (0.05). None of these phosphors yielded an observable spectrum.

Group five has as members: hex. $\text{ZnS}:\text{Cu}$ (0.3); cubic $\text{ZnS}:\text{Cu}$ (0.03); hex. $\text{ZnS}:\text{Cu}$ (0.003); cubic $\text{ZnS}:[\text{Zn}]$; cubic $\text{ZnAl}_2\text{O}_4:\text{Cr}$ (0.25); tricl. $\text{Ca}_2\text{MgSiO}_7:\text{Ce}$ (0.05) monocl. $\text{CaMg}(\text{SiO}_3)_2:\text{Ti}$ (0.02); $\text{Ca}_2\text{P}_2\text{O}_7:\text{Dy}$; $\text{ZnS}:\text{Cu}$ (0.1); $\text{ZnS}:\text{Cu}$ (0.3); $\text{ZnS}:\text{Cu}$ (2.0). These are all the nonmanganese activated phosphors investigated, and none of them yielded an observable spectrum.

INTERPRETATION

As a point of departure, we assume that, to a first approximation, we have free ions all of which exist in a common ground state in the absence of a field. When a steady magnetic field is applied, these ions will occupy $2J+1$ equally spaced Zeeman levels according to the

FIG. 3. Experimental record cub. $\text{ZnS}:\text{Mn}$ (0.001).

⁷ Twenty-six of the phosphor samples were furnished by H. W. Leverenz of RCA Laboratories and six by F. E. Williams of the General Electric Research Laboratory.

TABLE I. Calculated values for absorption lines of Mn-activated phosphors. Spectra display "hyperfine" structure only.

Material	$H_{5/2}$	$H_{3/2}$	$H_{1/2}$	$H_{-1/2}$	$H_{-3/2}$	$H_{-5/2}$	A	K	H_0	ν (Mc)	g
Cub. ZnS:Mn	3145.5	3211	3278	3346.5	3416.5	3488	68.5	0.75	3318.5	9290	2.0
Cub. ZnAl ₂ O ₄ :Mn	3116	3194	3274	3356	3440	3526	82	1.0	3324	9290	2.0
MgO:Mn(197-2)	3097	3181.5	3267.5	3355	3444	3534.5	87.5	0.75	3319	9290	2.0
MgO:Mn(200-2)	3138	3211	3286	3363	3442	3523	77	1.0	3333	9290	2.0

Accuracies: H : ± 1 gauss; A : ± 1 gauss; K : ± 0.05 gauss.

Boltzmann distribution. All transitions take place within the ground state of the ion, and adjacent levels are separated in energy by

$$\Delta E = g\beta H,$$

where g = spectroscopic splitting factor, β = Bohr magneton = $eh/4\pi mc$, and H = externally applied magnetic field.

If now a radiofrequency magnetic field of frequency ν impinges on the ions at right angles to the static field, the probability of an ion making a transition from the level it occupies to an adjacent level, is a maximum when the condition

$$h\nu = g\beta H$$

is satisfied. This is the magnetic resonance condition.

Transition probabilities to a higher and lower level are the same but the lower levels are more highly populated and there is, therefore, a greater absorption than emission. For usual microwave power values, the Boltzmann distribution is retained and there is a net absorption.

The "g" value of the paramagnetic ion can be determined from the values of the frequency, ν , and the magnetic field, H , at absorption.

When incorporated in a crystalline solid, the paramagnetic ion is subjected to strong internal electric fields. The major interactions to which the ion is then subject arise from

1. an internal electric field;
2. LS coupling;
3. external magnetic field;
4. electronic-nuclear spin interaction.

This interaction is proportional to the concentration and tends to broaden the sharply defined levels by producing a large number of close-lying neighboring

levels. It may be interpreted as arising from an internal magnetic field, whose value is not the same at all ions because of the statistical distribution of the paramagnetic ion dipole orientations. At the low concentrations used in this research, dipole-dipole broadening is negligible.

The second contribution is an exchange interaction between spin systems, which Van Vleck⁸ has shown tends to broaden an absorption line at the wings and sharpen its peak, or in effect, to narrow the line. This "exchange narrowing" may be looked upon as a rapid energy exchange between spin systems resulting in diminished localized or internal magnetic field spread. As is to be expected, the effect disappears at very dilute concentrations of the magnetic ion.

The third contribution is that of spin-lattice relaxation and is the mechanism by which an ion in an excited state returns to its unexcited state. When the relaxation occurs in an exceptionally short time, the energy level, and hence the absorption line, is broadened to such an extent as to make the spectrum unobservable. The mechanism of the relaxation process has been given by Kronig⁹ and Van Vleck¹⁰ as follows: Transfer of heat of magnetization between the magnetic spin system and the crystal lattice is provided by the Stark effect of the electric field of the lattice. The thermal vibrations of the crystal lattice produce periodic variations in the electric field acting on the ions which affect the energies of the orbital levels. Through spin-orbit coupling these effects provide an interaction between the spins and the lattice. Thus long relaxation times may be realized either by large crystal field splittings which break down LS coupling or by the use of low temperatures to reduce crystal lattice vibrations.

The fourth contribution to line width is anisotropy-energy broadening. For low symmetry crystal fields, the energy of a paramagnetic ion in a magnetic field

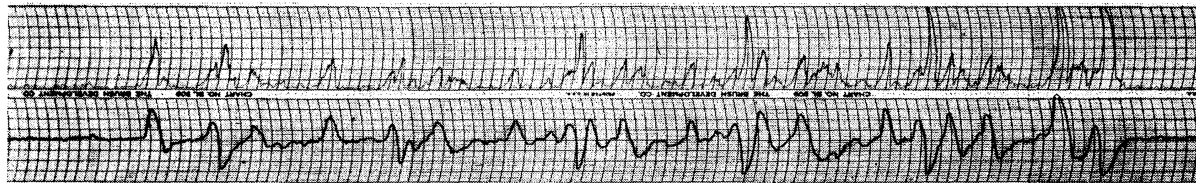


FIG. 5. Experimental record hex. ZnS:Mn (0.001).

⁸ J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

⁹ R. de L. Kronig, Physica 6, 33 (1939).

¹⁰ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

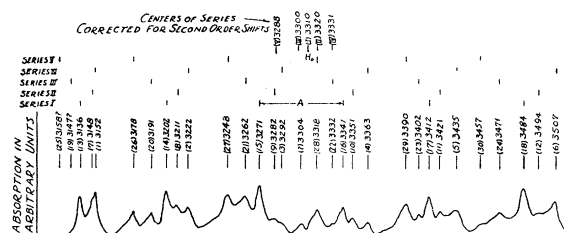


FIG. 6. Absorption of hex. ZnS:Mn (0.001).

is a function of the orientation of the crystal axis with respect to the external field. The angular dependence varies as $(3 \cos^2 \theta - 1)$.¹¹ If the material under investigation is a powder in which the crystal axes are oriented at random in a magnetic field, it is possible that the energy differences associated with the various orientations are sufficient to broaden the absorption lines to the extent that they are no longer observable.

MANGANESE PHOSPHORS

As indicated, Mn^{++} is of particular interest^{11,12} because it is, in many respects, the ideal paramagnetic substance; and further, the study has yielded certain unexpected results. Mn^{++} has five unpaired $3d$ -electrons, in addition to filled shells, with a total electron spin $S = 5/2$ and nuclear spin $I = 5/2$.

Its ground state is ${}^6S_{5/2}$, so the "quenching" of orbital angular momentum need not arise and it should behave very much as a free spin magnetic dipole. The crystal field can affect the electronic spin only indirectly through interaction with L and spin-orbit coupling. Since only second order spin-orbit coupling is present, the relaxation times should be long enough so that undue broadening of the magnetic resonance spectrum of Mn^{++} in any compound should not occur. The "g" factor should be isotropic and almost exactly 2. Similarly any crystal field splitting must necessarily be small and because of the spherical symmetry of the electronic distribution, there should be no electronic-nuclear spin interaction. Finally, electric quadrupole and external magnetic field-nuclear spin interactions are too small to be observable; this is so since, to the first order, they merely shift each of the hyperfine levels, becoming observable only under violation of the selection rule $\Delta m = 0$.

Experimentally, the most striking feature of the spectra is the existence of a pronounced isotropic hyperfine structure. Also the crystal field splitting is greater than would be expected from the symmetry of the field in which the Mn^{++} has been investigated.

In attempting to account for hyperfine structure where none is expected, the mechanism suggested thus far¹³ is that of an admixture to the $3s^2 3p^6 3d^5$ configura-

tion of a small fraction of a configuration in which one $3s$ -electron has been promoted to a $4s$ -state. The overall state is still assumed to be ${}^6S_{5/2}$ and to retain the parity of the main configuration. This mechanism would predict that the hyperfine structure is a property of the free ion and does not arise from the crystal field.

The crystal splitting (where it has appeared) has likewise been unexpected. To account for the relatively large splitting, it has been proposed¹³ that electric fields of axial symmetry in conjunction with spin-spin interaction may be expected to give rise to a second-order contribution to the Hamiltonian of the form $D[S_z^2 - \frac{1}{3}S(S+1)]$. The proposal is that the field produces a slight ellipsoidal deformation of the otherwise spherically symmetric electronic distribution and that then the mutual energy of the spin magnetic moments will no longer be isotropic but will depend upon their orientation relative to the symmetry axis. The cubic field may well still contribute; however, it is such a high order coupling as to have a coefficient small compared to the second-order process described. The direct interaction between the nuclear magnetic moment and the $3d$ electron shell which arises because of the proposed distortion of the electron distribution is very small and contributes at best a slight anisotropy to the hyperfine structure.

The Hamiltonian of the Mn^{++} system may be represented as follows:

$$\mathcal{H} = g\beta HS + D'[S_z^2 - \frac{1}{3}S(S+1)] + A'S \cdot I. \quad (1)$$

Here g is the spectroscopic splitting factor, β the Bohr magneton, H the external magnetic field, S the electron spin operator, and I the nuclear spin operator. The first term denotes the interaction between external magnetic field and magnetic moment of electron spin, and in fields of the order of 3000 gauss, it is the dominant term.

The energy levels for each M and m (magnetic quantum numbers of electronic and nuclear spin, respectively) are

$$E_{M,m} = g\beta HM + D'[M^2 - \frac{1}{3}S(S+1)] + A'Mm + K'\{M[I(I+1) - m^2] - m[S(S+1) - M^2]\}.$$

The last term is the result of a second-order perturbation calculation on the term $A'S \cdot I$ where K' is given by $A'^2/2h\nu$. Figure 7 illustrates this over-all splitting and resultant absorption spectrum.

Since the selection rules for absorption are $\Delta M = 1$, $\Delta m = 0$, the energy difference, rearranged in terms of gauss, is

$$H = H_0 - D(2M-1) - Am - K[I(I+1) - m^2], \quad (2)$$

where $H_0 = h\nu/g\beta$, while D , A and K are D' , A' and K' divided by $g\beta$ respectively. A term $-Km(2M-1)$ has been neglected, since the resultant splitting is less than the line width and the center of gravity remains unchanged.

¹¹ B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

¹² E. E. Schneider and T. S. England, Physica **XVII**, 221 (1951).

¹³ A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

Group One

The spectra of group one correspond to transitions between the unperturbed Zeeman levels, $g\beta HM$, and have a width so large as to make other effects unobservable.

Since the concentration of paramagnetic ions in the phosphors is very low, the broadening arising from dipole-dipole interaction may be neglected. Further, since the ions are all Mn^{++} , LS coupling is small and the spin-lattice relaxation times too long to broaden the spectra significantly. The major contribution to the line width arises from the anisotropy energy broadening of the relatively low symmetry crystals in powdered form. This is borne out by the resolution in groups two and three where the crystal symmetries are high. The "g" values are all very nearly 2, in agreement with the ions being in an S ground state.

Group Two

The spectra of group two phosphors, corresponding to transitions between the shifted hyperfine levels are given by Eq. (2) neglecting the term $D(2M-1)$. The crystal symmetries are high so there is no undue anisotropy broadening but also no crystal field splitting.

Table I indicates the fit of theory with experiment and the values of the constants involved. Of note, is the variation in the value of the hyperfine splitting constant which is not in quantitative agreement with the mechanism proposed¹³ to account for the splitting.

The spectra of this group are consistent with the spin of the manganese nucleus of $5/2$.

Group Three

The spectra of these two phosphors correspond to transitions as given by Eq. (2) and shown in Fig. 7. The crystal symmetries are slightly lower than those of group two—sufficiently lower to produce crystal field splitting but not low enough to broaden the spectra unduly.

The five series (fine structure) of six unequally spaced hyperfine lines for the spectrum of Fig. 6 are tabulated in Table II showing the fit of theory with experiment and giving the values of the constants involved.

TABLE II. Calculated values for absorption lines of Mn-activated phosphors. Spectra display both "fine" and "hyperfine" structure.
 $H = H_0 - D(2M - 1) - Am - K[I(I + 1) - m^2](2)$
 Hex. ZnS:Mn.

Series I	Series II		Series III		Series IV		Series V	
$M = \frac{1}{2} \rightarrow \frac{1}{2}$	$M = \frac{1}{2} \rightarrow \frac{3}{2}$	2D	$M = \frac{3}{2} \rightarrow \frac{1}{2}$	2D	$M = \frac{3}{2} \rightarrow \frac{5}{2}$	4D	$M = \frac{5}{2} \rightarrow \frac{3}{2}$	4D
$H_{13} = 3136$	$H_7 = 3148$	12	$H_{10} = ?$?	$H_1 = 3152$	16	$H_{25} = ?$??
$H_{14} = 3202$	$H_8 = 3211$	9	$H_{20} = 3191$	11	$H_2 = 3222$	20	$H_{26} = 3178$	24
$H_{15} = 3271$	$H_9 = 3282$	11	$H_{21} = 3262$	9	$H_3 = 3292$	21	$H_{27} = 3248$	23
$H_{16} = 3341$	$H_{10} = 3351$	10	$H_{22} = 3332$	9	$H_4 = 3363$	22	$H_{28} = 3318$	23
$H_{17} = 3412$	$H_{11} = 3421$	10	$H_{23} = 3402$	9	$H_5 = 3435$	24	$H_{29} = 3390$	21
$H_{18} = 3484$	$H_{12} = 3494$	10	$H_{24} = 3471$	11	$H_6 = 3507$	23	$H_{30} = 3457$	27
			$A = 70 \pm 1$ gauss;		$H_0 = 3310 \pm 1$ gauss;			
			$K = 0.5 \pm 0.05$ gauss;		$g = 2.0 \pm 0.05$;			
			Average $D = 5$ gauss.					

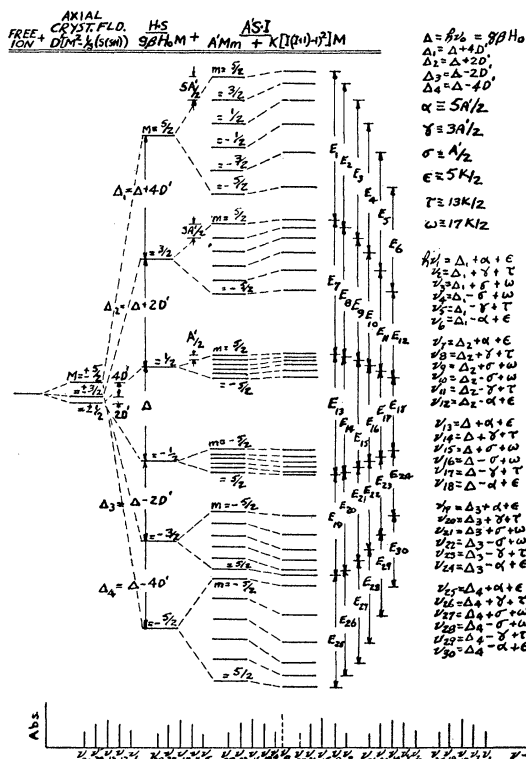


FIG. 7. Energy level diagram hex. ZnS:Mn.

Group Four

All members of group four are manganese activated phosphors yielding no observable spectra. Since all crystal symmetries are low, the lack of spectra has been attributed to the anisotropy broadening of the powdered samples. In general, phosphors are not available in single crystals as a result of the methods currently in use in making them, but studies with such crystals would be useful in furnishing further checks on the correctness of the present interpretation.

NONMANGANESE PHOSPHORS

Group Five

The iron group members of group five with the exception of Ti^{+++} all exist in high symmetry crystal

fields. Since none are in an S ground state, their orbital angular momenta will be incompletely "quenched" and their spin-lattice relaxation times correspondingly short. The rare earth members have a strong LS coupling in any event, because of the shielding about the $4f$ -shell, and have similarly short spin-lattice relaxation times. It is, therefore, not surprising that at room temperature the spectra should be unobservable because of such broadening. Ti^{+++} is in a low symmetry field, which lengthens the relaxation time but broadens the spectrum because of its powdered form.

VALENCY CONSIDERATIONS

An alternative mechanism may exist for the lack of spectra with copper activated phosphors. It is the possibility of copper existing as Cu^+ rather than Cu^{++} . Cu^+ has only filled shells and is not paramagnetic. The evidence is not conclusive that this is the case; however, other investigations¹⁴ have suggested this possibility on purely optical and chemical grounds.

Of a more definite character is the difference in magnetic spectra between the phosphors $MgO:Mn(197-2)$ and $MgO:Mn(200-2)$. These phosphors are identical in composition, concentration and presumably crystal structure. They differ in luminescence spectra, and it was suspected on that basis that No. 197-2 contains only Mn^{++} while No. 200-2 contains 20 percent Mn^{++} and 80 percent Mn^{4+} . Arguing that Mn^{4+} will not yield an observable spectrum because of a short spin-lattice relaxation time (see Cr^{+++}), the ratio of spectra magnitudes of 10:1 indicates that No. 200-2 contains 10 percent Mn^{++} and 90 percent Mn^{4+} , in close agreement with expectations from luminescence data. In short, paramagnetic spectra may well prove useful, in conjunction with other data, in determining the valence state of paramagnetic ions dissolved in a host material.

¹⁴ R. H. Bube, J. Chem. Phys. 19, 985 (1951).

CRYSTAL STRUCTURE AND SPECTRA

In this research, manganese was available as an activator in low concentrations in both cubic zinc sulfide and hexagonal zinc sulfide giving rise to markedly different spectra as shown in Figs. 4 and 6. Such evidence serves to illustrate the utility of the method of paramagnetic resonance for determining crystal structure. A spectrum similar to that shown in Fig. 6 was reported by Schneider and England¹⁴ for manganese in zinc sulfide, but no indication was given of the crystal structure. It seems reasonable to suspect that the material used by these English workers was hexagonal or a mixture of cubic and hexagonal crystals. At least this hypothesis makes their results consistent with those reported here.

SUMMARY

The work with dilute paramagnetic materials outlined above demonstrates to some degree the utility as well as the limitations of the paramagnetic resonance method. Much of the information we now have on electrons in solids depends upon their mobility and in many cases on surface conditions, as in thermionic and photoelectric emission and in contact rectifiers. On the contrary, in the paramagnetic resonance method, electron mobility may sometimes be an experimental handicap, and, in any event, the electrons seen by the method make themselves known solely by their spin and magnetic moment. Deep-lying rather than surface electrons are seen and the interactions between spin and environment which give rise to anomalous g -values, to line broadening, and to "fine" and "hyperfine" structure yield a fund of information on the fields inside of a material, as well as the valence state of an ion for which the paramagnetic effects are observed.