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Interaction of Manganese Activator Ions in Zinc-Orthosilicate Phosphors

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A study was made of specially prepared rhombohedral Zn_2SiO_4:Mn phosphors, utilizing magnetic, chemical, and luminescence techniques. From measurements of Weiss constants, it is shown that magnetic interaction occurs between manganese activator ions. The magnetic interaction increases with increasing proportion of manganese in the range where the following related luminescence characteristics decrease: (1) efficiency, (2) temperature break-point, and (3) decay time.

An analysis of the magnetic data shows that isolated noninteracting manganese activator ions have five unpaired electrons, corresponding to Mn^{2+}, and $\bar{\mu}=5.90$ Bohr magnetons (5.92 theoretical).

The molar diamagnetic susceptibility of zinc-orthosilicate was determined as being $(-64.6\pm0.7)\times10^{-6}$.

I. INTRODUCTION

URBAIN,[1] in 1908, first proposed the so-called "law of the optimum" in luminescence, that an optimum activator concentration exists for maximum luminescence emission intensity. Perrin[2] proposed that the decrease in luminescence emission intensity at higher activator concentrations was due to "overlapping fields" of pairs of activators in close proximity, and that such proximity caused coupling, with a concomitant decrease in the ability of the centers to be excited.

The interaction of activator ions has been assumed by several investigators[3–5] for various phosphor systems. Recently, Johnson and Williams have attempted to interpret the dependence of luminescence on activator concentration.[6]

The problem of interaction of manganese activator ions in zinc-orthosilicate and their relation to luminescence was attacked by a combination of magnetic, luminescence, and chemical procedures. Little work has been reported on the magnetic properties of oxygen-dominated phosphors. Johnson and Williams[7] have reported a small decrease in paramagnetic susceptibility on exciting zinc-orthosilicate:Mn, and Spencer *et al.*[8] have investigated the paramagnetic resonance line width of zinc-orthosilicate:Mn.

II. EXPERIMENTAL METHODS

Magnetic

The Gouy method of determining magnetic susceptibility was used.[9] The electromagnet current was supplied by a motor-generator, and the current was varied by adjusting a series of variable resistors. A Christian Becker analytical balance, with a sensitivity of 0.1 milligram, was used, the analytical weights having been checked by the National Bureau of Standards.

The low temperature unit, as shown in Fig. 1, was constructed from a solid block of magnesium-aluminum alloy. The diameter of the widest portion was $1\frac{5}{8}$ in. A channel, $\frac{9}{16}$-in. in diameter, was machined through the center of the block for the sample-tube suspension. A $\frac{1}{8}$-in. channel, $\frac{7}{8}$-in. deep, in the solid portion of the block, accommodated the thermocouple. In order to provide for an inert atmosphere, a groove extending from top to bottom of the main channel was cut, and a cylindrical aluminum sleeve was force-fitted into the channel. A copper tube, through a threaded connection, made contact with the groove, and was used for the gas inlet, while the outlet was the main channel. To provide for temperature variation, several turns of Nichrome wire were wound about the neck of the unit, using asbestos tape as insulation. The temperature of the unit was measured with a calibrated copper-constantan thermocouple, in conjunction with a dc millivoltmeter, which could be read to 0.05 millivolt. A special Dewar flask with completely silvered inner surface was constructed of Pyrex glass, and was shaped to fit between the pole pieces of the magnet.

The sample tubes were made from very thin-walled Pyrex glass, the cross-sectional areas being obtained by calibration with boiled distilled water. A Nylon thread was used for the suspension of the sample, and in order to avoid errors due to air currents, the thread was enclosed in a Bakelite tube. Errors in powder packing were minimized by gravimetrically determining the apparent density for each case.

The electromagnet field strength as a function of current was calibrated with (1) Mohr's salt, $FeSO_4$-$(NH_4)_2SO_4\cdot6H_2O$,[10] as the ground powder;[11] (2) manga-

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[1] G. Urbain, Compt. rend. **147**, 1472 (1908).

[2] J. Perrin, Ann. phys. **11**, 5 (1919).

[3] F. A. Kroeger, dissertation, J. Van Campen, Amsterdam, 1940.

[4] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **28**, 171 (1935).

[5] Z. A. Trapezinkova, Doklady Akad. Nauk S.S.S.R. **74**, 465 (1950).

[6] P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 1477 (1950); Phys. Rev. **81**, 146 (1951).

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

[8] Spencer, Garstens, Klick, and Schulman, J. Chem. Phys. **20**, 1177 (1952).

[9] See, for example, P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943).

[10] L. C. Jackson, Trans. Roy. Soc. (London) **A224**, 1 (1923).

[11] It was first established that no ferromagnetic impurities were present, and that grinding did not affect the magnetic susceptibility.

nese sulfate, $MnSO_4 \cdot 4H_2O$;[12] (3) triple-distilled water, boiled free of dissolved air.[13]

Readings were taken at intervals from liquid-nitrogen temperature to room temperature, the gas flow being stopped for each reading. By substituting the appropriate values in the Gouy equation,[9] the specific susceptibility at each temperature is obtained, and this is converted to molar susceptibility.

Chemical

Synthesis of Phosphors

The ingredients used in synthesizing the phosphors consisted of a selected lot of J. T. Baker's analytical-grade zinc oxide, and an "ultrapure" silicic acid (obtained from the Mallinckrodt Chemical Company) which contained 11.9 percent water. The absence of appreciable amounts of metallic impurities in the ingredients was determined in two ways: (1) spectrographic analyses, and (2) luminescence analyses. The latter were performed by conversion of the zinc oxide to an unactivated zinc sulfide phosphor. The intense blue luminescence emission showed the absence of "poison" ions, such as iron, cobalt, nickel in appreciable amounts. Similarly, the silicic acid, when fired, showed the characteristic blue emission of pure fired silica.

Weighed amounts of the ingredients, to yield the orthosilicate,[14] were dry-ball-milled for 24 hours, to insure homogeneity. Manganese, as a solution of the nitrate, was added to give desired concentrations, additional silica having originally been added for reaction with the manganese.

The materials were slurried with triple-distilled water, and dried at 125°C. The mixes were then transferred to platinum crucibles, and the series was fired in air at 1280°C, for four hours, in a Globar-type, temperature-controlled furnace. Only the cores of the phosphor cakes were used, and no grinding was done.

Analytical

In determining the susceptibility of the phosphors, it is essential that the final manganese proportion be known. For example, Rupp[15] found a 20 percent loss of manganese after firing zinc sulfide:Mn. Weighed portions of zinc-orthosilicate:Mn phosphors were dissolved in concentrated hydrofluoric acid, and the bismuthate method[16] was used, manganese being determined colorimetrically as permanganate.

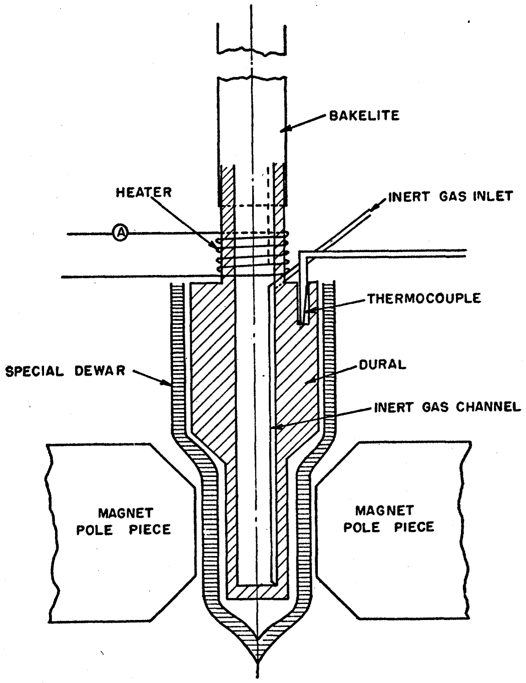

FIG. 1. Low temperature susceptibility unit.

To determine the amount of manganese in higher oxidation states, the iodometric method of Gossner and Bruckl[17] was modified and used. The reagents were standardized and a "blank" of zinc-orthosilicate with no added manganese was used.

Luminescence

Spectral Distribution

Curves of spectral distribution were obtained with a recording spectroradiometer,[18] the phosphor being prepared as a thick patch.[19] Excitation of the phosphor in a demountable cathode-ray tube was by 10-kilovolt electrons, as a dc spot, with a current density of 13 microamperes/cm^2.

Emission Intensity and Decay

Relative integrated luminescence emission intensities were obtained, using a demountable cathode-ray tube, and a 1P21 phototube. The phosphors were excited by an electron beam, and both low (1 μa/cm^2) and high (100 μa/cm^2) current densities were used.

Decay curves, after excitation by cathode rays, were obtained with a dc oscillograph-phosphoroscope.

III. EXPERIMENTAL RESULTS

Test for Ferromagnetic Impurities

The zinc-orthosilicate:Mn phosphors were shown magnetically to be free of contamination by traces of

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[12] L. F. Bates, *Modern Magnetism* (Cambridge University Press, London, 1948), second edition, p. 130.

[13] S. Seely, Phys. Rev. **49**, 812 (1936).

[14] Zinc-orthosilicate, Zn_2SiO_4, is the only true compound in the system ZnO-SiO_2, as shown by the phase studies of E. N. Bunting, J. Research Natl. Bur. Standards **4**, 131 (1930).

[15] E. Rupp, Ann. Physik **78**, 505 (1925). The loss of manganese reported by Rupp has been traced to volatilization of manganese chloride at the crystallization temperature for hexagonal zinc sulfide.

[16] Described in, for example, I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Chemistry* (Macmillan Company, New York, 1948), revised edition, p. 755.

[17] G. Gossner and K. Bruckl, Zentr. Mineral. T. I 316 (1928).

[18] V. K. Zworykin, J. Opt. Soc. Am. **29**, 84 (1939).

[19] Measurements were made by R. H. Bube and R. E. Shrader.

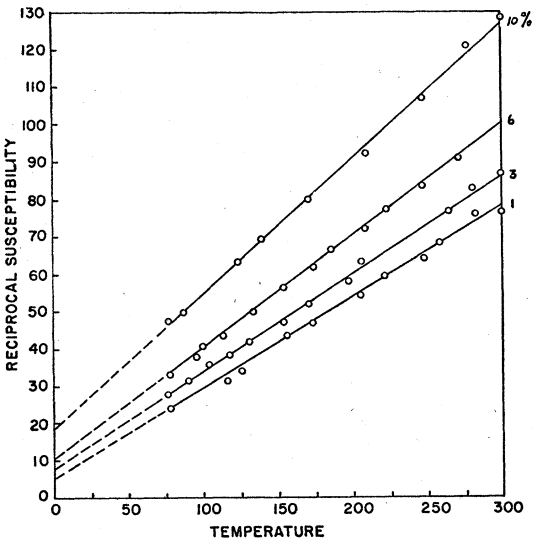

FIG. 2. Reciprocal paramagnetic susceptibility as a function of temperature of zinc-orthosilicate:Mn phosphors, with indicated proportions of manganese.

ferromagnetic impurities, by measuring the weight change as a function of magnetic field strength, H. The change in weight, Δw, was found to vary linearly with H^2, as predicted by the Gouy relation,

$$g\Delta w = \tfrac{1}{2}kAH^2, \qquad (1)$$

g, k, and A being constants.

Diamagnetic Susceptibility of Unactivated Zinc-Orthosilicate

The luminescent materials under investigation consist of diamagnetic zinc-orthosilicates, in which small amounts of paramagnetic manganese ions have been incorporated. The problem of susceptibility determinations in such cases has been discussed by Haller and Selwood[20] for the case of trivalent cerium in lanthanum oxide.

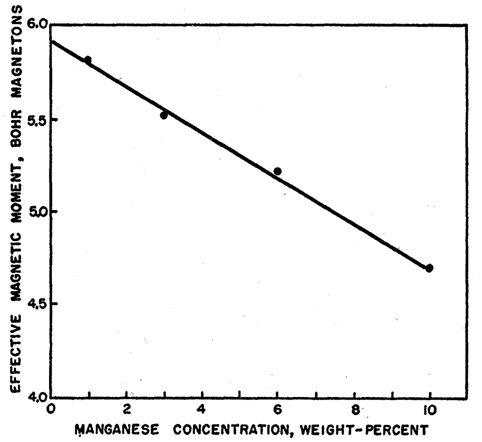

FIG. 3. Effective magnetic moment as a function of the proportion of manganese in zinc-orthosilicate phosphors.

The diamagnetic susceptibility of unactivated zinc-orthosilicate was determined from the loss in weight. The value obtained for the specific susceptibility was $-(0.289 \pm 0.003) \times 10^{-6}$, corrected for the slight contribution of the Pyrex container. The susceptibility was found to be independent of temperature in the range 77°–300°K.

No previous determination of the susceptibility of zinc-orthosilicate has been found in the literature. It is interesting, however, to compare the above value with those reported by various investigators for other oxygen-dominated, zinc-containing materials: thus, for zinc oxide, -0.26×10^{-6} and -0.33×10^{-6} have been reported, and for zinc sulfate, -0.27×10^{-6} and -0.53×10^{-6} have been reported.[21]

IV. MAGNETIC PROPERTIES AS A FUNCTION OF MANGANESE CONTENT

It was found, for zinc-orthosilicate phosphors, with manganese in the range from one to ten percent by weight, that the Curie-Weiss law was followed:

$$\chi = C/(T+\Delta) \qquad (2)$$

TABLE I. Curie and Weiss constants as a function of manganese proportion.

% Mn	C	Δ
1	4.16	16
3	3.84	27
6	3.45	38
10	2.78	57

where χ is the molar susceptibility, C is the Curie constant, T is the absolute temperature, and Δ is the Weiss constant.

The reciprocal susceptibility as a function of temperature is shown in Fig. 2, from which it is seen that both the slope and intercept vary with manganese concentration. Table I illustrates the dependence of the Curie and Weiss constants on the manganese proportion. It is found that the Curie constant decreases with increasing manganese proportion whereas the Weiss constant increases.

Effective Magnetic Moments

The effective magnetic moments, μ_{eff}, in Bohr magnetons were calculated from the relationship:

$$\mu_{\text{eff}} = 2.84[\chi(T+\Delta)]^{\frac{1}{2}}. \qquad (3)$$

It was found that μ_{eff} decreases monotonically with increasing manganese content, as is shown in Fig. 3. Extrapolation to the region of infinite magnetic dilution

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[20] R. B. Haller and P. W. Selwood, J. Am. Chem. Soc. **61**, 85 (1939).

[21] Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (Springer, Berlin, 1923), p. 1245.

yields the value of 5.90 Bohr magnetons, as against the theoretical "spin-only" value of 5.92 Bohr magnetons for Mn^{2+}. Other investigators have reported values of 5.2 to 5.96 Bohr magnetons for manganous salts.[22]

V. LUMINESCENCE OF ZINC-ORTHOSILICATE:Mn PHOSPHORS

Spectral Distribution

Spectral distribution curves for zinc-orthosilicate with one percent manganese and with ten percent manganese are shown in Fig. 4, and are similar to those previously reported.[23] The phosphor with one percent manganese (Curve 1) has an emission whose peak wavelength occurs at 5250A. The effects of increasing the manganese to ten percent (Curve 2) are: (1) the short-wavelength limit of the spectral-distribution curve shifts to 4900A, whereas it occurs at 4750A for the sample with one percent manganese; (2) the peak wavelength is at 5350A; (3) the long-wavelength limit occurs at 6300A.

Luminescence Emission Intensity and Decay

Figure 5 shows the relative emission intensities as a function of manganese proportion. For the low current density, the maximum emission intensity occurs at 0.1 percent manganese, while with the higher current density, the optimum occurred at one percent manganese.

TABLE II. Decay characteristics of zinc-orthosilicate:Mn phosphors, with low and high current density excitation.

% Mn	τ (millisec) Low c.d.	High c.d.
0.01	13.3	12.8
0.1	13.3	11.2
1.0	9.1	7.4
10	1.1	3.9

Decay characteristics after excitation by cathode rays are summarized in Table II, for manganese concentrations ranging from 0.01 to 10 percent.

There is apparently no effect on τ, for low current density, until at least 0.1 percent manganese, after which there is a sharp decrease in τ with increasing manganese. With high current density excitation, τ decreases with increasing manganese content from 0.01 percent manganese.

VI. CHEMICAL AND X-RAY ANALYSES

In contrast to the report of Rupp,[15] concerning the loss of manganese on firing zinc-sulfide:Mn, it was found on chemical analysis that the manganese remaining in zinc-orthosilicate, after the crystallization firing, in no case deviated by more than 0.5 percent from the amount used in the synthesis. The calculations of susceptibility are based on the actual amounts of manganese found to be present in the phosphors.

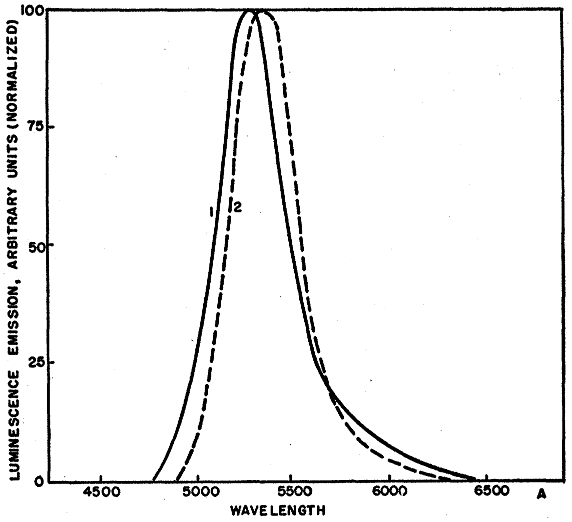

FIG. 4. Cathodoluminescence spectral distribution curves for zinc-orthosilicate phosphors with 1 and 10 percent manganese.

Determination of the amount of manganese in higher oxidation states gave the following results: (1) no manganese existing in a higher oxidation state was found in the sample with 0.1 percent manganese; (2) the phosphors with 1, 3, 6, and 10 percent manganese showed higher valence manganese present only in the amount of 0.03 percent of the manganese in the one percent sample, to 1.02 percent of the manganese in the ten percent sample.

The phosphors became increasingly brown to daylight with increasing amounts of manganese. This has been previously observed with zinc-beryllium-silicate:Mn phosphors by Froelich,[24] who attributed the effect to a brown oxide, probably Mn_2O_3, formed at the surface.

X-ray powder diffraction patterns of the phosphors[25] indicated a high degree of crystallinity, as well as solid

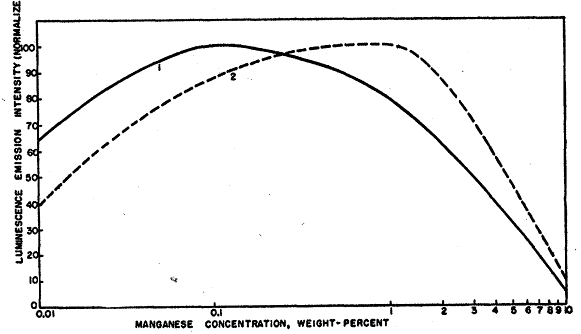

FIG. 5. Relative cathodoluminescence emission intensity of zinc-orthosilicate:Mn, at high (2) and low (1) current densities, as a function of manganese proportion.

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[22] See reference 9, p. 99.

[23] H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), p. 225.

[24] H. C. Froelich, Trans. Electrochem. Soc. **87**, 429 (1945).

[25] Taken by I. J. Hegyi.

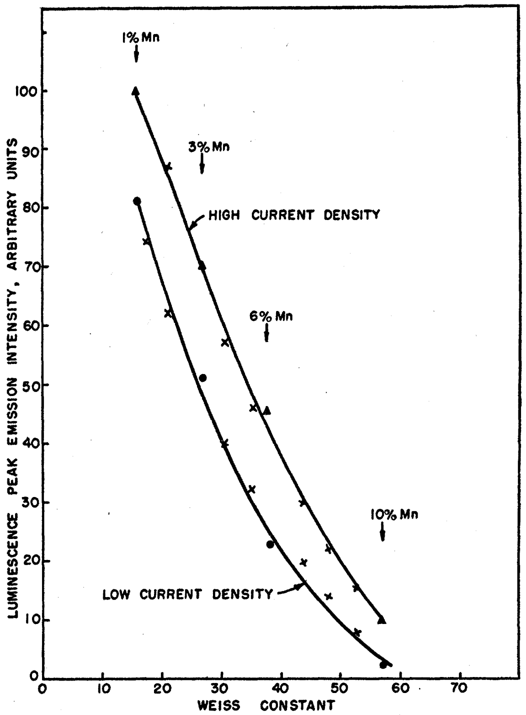

FIG. 6. Cathodoluminescence emission intensity of zinc-orthosilicate: Mn phosphors as a function of the Weiss constant.

solution of the zinc and manganese silicates, in agreement with the work of Kröger.[3]

VII. DISCUSSION

Diamagnetism of Zinc-Orthosilicate

Various attempts have been made to calculate ionic diamagnetic susceptibilities from quantum-mechanical considerations. Pauling[26] has derived the following expression for diamagnetic susceptibility:

$$\chi = 2.010\times10^{-6}\sum\frac{n^4}{(Z-S)^2}\left\{\frac{1-3l(l+1)-1}{5n^2}\right\}, \quad (4)$$

where Z is the nuclear charge, S is a screening constant, and n and l are quantum numbers. Slater[27] obtains for the diamagnetic susceptibility of each electron in a group

$$\chi = -0.807\times10^{-6}(n^*)^2(n^*+\tfrac{1}{2})(n^*+1)/(Z-S)^2. \quad (5)$$

Angus[28] has modified the Slater method, so as to separate s and p electrons having the same quantum number.

Calculated ionic diamagnetic susceptibilities for oxygen, zinc and silicon ions using the methods of Pauling (L.P.), Slater (J.C.S.) and Angus (W.R.A.) are given in Table III.[29]

Assuming additivity, the diamagnetic susceptibility of zinc-orthosilicate, Zn_2SiO_4, can be calculated. The values obtained, using the various methods, are listed in Table III.

Agreement between calculated and experimental values is good, considering the complexity of the compound involved. The method of Pauling is closest to the experimental value, and it is also indicated that when s and p electrons of the same quantum number are considered separately (Angus), the resulting calculated susceptibility is closer to the actual experimental value.[30]

The Ionization State of Manganese in Zinc-Orthosilicate

The evidence heretofore for the ionization state of manganese in zinc-orthosilicate has been rather indirect in nature, and has been summarized by Kroeger.[31]

The present investigation corroborates the chemical findings, in that only inappreciable amounts of higher-valency manganese were found. In addition the magnetic findings indicate the presence of manganese ions with five unpaired electrons, since at infinite magnetic dilution, a moment of 5.90 Bohr magnetons was obtained, as compared to the theoretical "spin-only" moment of 5.92 Bohr magnetons for a doubly ionized manganese ion.

Magnetic Interaction of Manganese Activator Ions

That magnetic interaction occurs among the manganese activator ions in zinc-orthosilicate has been shown by (1) the decrease in the Weiss constant with decreasing amounts of manganese, and (2) the decrease in the effective magnetic moment with increasing manganese proportion.

Calculated magnetic moments, based on probability considerations of having only isolated manganese ions

TABLE III. Comparison of calculated and experimental values of diamagnetic susceptibility of zinc-orthosilicate ($-\chi\times10^6$).

	L.P.	J.C.S.	W.R.A.	Exptl.
$O^{=}$	12.6	13.15	11.25	
Zn^{++}	11	15.57	15.45	
Si^{++++}	2.1	2.03	1.87	
Zn_2SiO_4	74.5	85.77	77.77	64.6

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[26] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

[27] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[28] W. R. Angus, Proc. Roy. Soc. (London) **A136**, 569 (1932).

[29] Values from Angus, reference 28.

[30] The empirical method of P. Pascal, Ann. chim. phys. **19**, 5 (1910), useful for organic compounds, gives a calculated value (probably fortuitous) close to the experimental value. If the Pascal constants for zinc (-13.5×10^{-6}), silicon (-20×10^{-6}), and carboxylic oxygen (-3.36×10^{-6}) are applied to zinc-orthosilicate, taking the constitutive correction as zero, the resulting calculated molar diamagnetic susceptibility is -60×10^{-6}. The value for carboxylic oxygen is used, as it is felt that this approximates most closely the resonance between silicon and oxygen in the orthosilicate radical.

[31] F. A. Kroeger, Trans. Electrochem. Soc. **95**, 356 (1949).

in zinc-orthosilicate[32] contributing to the moment, are lower than the experimentally determined values. These discrepancies can be accounted for by assuming (1) incomplete spin-pairing of pairs and clusters of manganese ions, with resultant contributions to the magnetic moment, or (2) that the distribution of manganese activator ions in zinc-orthosilicate is not of a random nature.

Interaction and Luminescence

If the decrease in luminescence emission intensity with increasing manganese proportion were due only to a decrease in the effective number of emitting centers, then neither the temperature break-point nor the lifetime of the excited state should be affected. However, the fact that both break-point and lifetime are functions of the manganese proportion can be explained by activator interactions which cause an increase in the probability of radiationless transitions. Figure 6 shows the relationship between emission intensity and the Weiss constant, under electron excitation, with high and low current density, for manganese proportions from 1 to 10 percent. It is seen that the decrease in emission intensity occurs for the same range of Mn proportion as the increase in the Weiss constant.

The effectiveness of the magnetic method for determining the ionization state and degree of interaction of small amounts of paramagnetic impurities should prove of value in studies of other systems, as well as in trapping, and the effect of luminescence poisons.

The authors wish to express their appreciation to H. W. Leverenz of the RCA Laboratories for his interest and encouragement, and to Dr. R. H. Bube for valuable discussions.

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[32] By *isolated* is meant having no manganese ion in next-adjacent available site; see H. W. Leverenz, reference 23, pp. 477–480. P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 323 (1950), assumed for ZnF_2:Mn phosphors that only those manganese ions which do not have other manganese ions at nearest cation sites are capable of luminescing. See also H. W. Leverenz and D. O. North, Phys. Rev. **85**, 930 (1952).

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The Evaluation of the Energy Matrix of the Tensor Forces

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It is shown how the use of tensor operators enables a simple calculation of the tensor forces in nuclear configurations by the usual spectroscopic methods. The number of independent parameters necessary to define the energy in the nuclear configuration l^n (or j^n) is found to be $2l$ (or $2j$), whereas it is shown to be only $[4l/3]$ (or $[2j+2/3]$) in the l^n (or j^n) configuration of equivalent nucleons. The energy matrix is given by means of a closed formula for the case of d^n and $(d_{5/2})^n$ configurations (of equivalent nucleons). It is found that in the latter configuration the order of levels for a short-range potential (of the tensor forces) is the same as for short-range central forces.

I. INTRODUCTION

IN a recent paper[1] it has been shown that the tensor forces possess the pairing property, i.e., this interaction is diagonal with respect to the seniority v and the term values of the configuration l^n (or j^n) of equivalent nucleons differ from the corresponding states of the l^v (or j^v) configuration only by the term $\frac{1}{2}(n-v)E_0$. E_0 is the energy of $l^2\,{}^1S$, which vanishes for tensor forces (or $j^2, J=0$). The proof of this fact is based on an expansion of the tensor force interaction between two nucleons into a sum of products of double tensors $\mathbf{s}_1\mathbf{C}_1^{(k)}$ and $\mathbf{s}_2\mathbf{C}_2^{(k)}$ of the two nucleons, where $\mathbf{s}_i$ is the spin vector of the ith nucleon and $\mathbf{C}_{ig}^{(k)}$ differ only by a constant factor from the spherical harmonics of order k which depend on the coordinates of the ith nucleon. This expansion will be used throughout this paper in order to obtain further results on the tensor forces.

The matrix elements of the tensor force interaction were calculated in the case of d^2 and p^2 by Marvin,[2] who took for the potential the special case of $1/r^3$ (which appears in the electromagnetic spin-spin interaction). The results of his long and complicated calculations are very simple, they contain only two independent parameters in the case of d^2 (and only one for p^2). Also, these parameters can be easily expressed by the ordinary Slater coefficients of the potential $1/r^3$. The decomposition described above enables a simpler calculation of the matrix elements of the tensor forces. We shall use a general potential and see to what cause the simplification which occurs in Marvin's results is due. The method used offers a natural definition of the radial parameters for the tensor forces, with the help of which

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[1] G. Racah and I. Talmi, Physica (to be published).

[2] H. H. Marvin, Phys. Rev. **71**, 102 (1947).