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The specific magnetic susceptibilities of manganese-activated zinc fluoride phosphors of diverse activator concentration, and prepared by various crystallization procedures, have been measured from −60°C to 200°C. A trivial Weiss constant, except for phosphors of inordinately high manganese concentration, demonstrates the absence of appreciable exchange demagnetization of adjacent paramagnetic activator ions and suggests that there exists negligible departure from a random distribution of manganese ions over cation sites. Utilizing this distribution, and recognizing that only manganese ions not having other manganese ions at any of the nearest cation sites are capable of luminescence, an expression for the dependence of luminescent efficiency on activator concentration is derived and found to be in quantitative agreement with experiment.

INTRODUCTION

IN previously reported work[1] on the magnetic properties of manganese-activated zinc fluoride, it was found that there exists a difference in multiplicity between the unexcited and the emitting states of the activator. Preliminary specific susceptibility measurements indicated that the unexcited activator is predominantly in the divalent state of maximum multiplicity, most probably the ^6S state. The susceptibility of one phosphor of moderate activator concentration was slightly below the theoretical value; and this fact was tentatively interpreted as being evidence for exchange demagnetization. Since the possibility of exchange interaction and a resulting departure from the random distribution of activator would be of considerable importance to the understanding of luminescence phenomena, and in particular to the problem of explaining luminescent efficiency as a function of activator concentration, it was decided to study the problem in greater detail.

TEMPERATURE DEPENDENCE OF MAGNETIC SUSCEPTIBILITY

First, the magnetic susceptibilities of a number of ZnF_2:Mn phosphors of various activator concentrations were measured as a function of temperature in order to determine the Weiss constant, which is a direct measure of the interaction energy. Measurements were made from −60°C to +200°C by use of the Gouy method.[2] Since only the Weiss constant and not the precise absolute susceptibility is needed, the only data required are the temperature dependence of the force on the sample produced by its interaction with the magnetic field. The observed forces are corrected for the non-

temperature dependent diamagnetic susceptibility of the host lattice, and that of the Pyrex sample tube. The experimental procedure eliminated the effect of the change in buoyancy of air with temperature. The sample tube, half-filled with the tightly packed powdered phosphor, was thoroughly flushed out with carbon dioxide, whose volume susceptibility is negligible, before being sealed. The temperature was measured by a calibrated thermocouple and controlled, by use of an electrically heated oven and a Variac to within 0.5°C in the range from 20° to 200°C. Measurements near −60°C were obtained by using dry ice-acetone-water as a coolant. Provision was made for the continual circulation of coolant in the jacket surrounding the chamber in which the sample was suspended.

Figure 1 shows the corrected results of the measurements. For convenience the molar susceptibility of the activator in each phosphor is normalized at 20°C to the theoretical "spin only" value for divalent manganese, and the ordinate scale is displaced for each phosphor. The force, f, on a sample using the Gouy method is given by the relation:[2]

$$f = \tfrac{1}{2}(k_1 - k_2)(H_1^2 - H_2^2)A,$$

where k_1 and k_2 are the volume susceptibilities of the sample and the surrounding atmosphere, respectively. H_1 is the maximum field located at one end of the sample, and H_2 is the minimum field located at the other. A is the cross-sectional area of the sample. Since k_2 is negligible, and H_1, H_2, and A are constant in a series of measurements, the force on the sample at a given temperature resulting from the interaction of the sample with the applied field is proportional to the volume susceptibility at that temperature. The volume susceptibility is proportional to the molar susceptibility because there is negligible change in density of the sample with temperature.

The 0.97 ZnF_2:0.034 MnF_2 was prepared by fusion in a "glow bar" furnace for 45 min. The other samples were prepared by fusion of the ingredients in an atmosphere of ammonium fluoride for 5 min. and allowed to

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

[2] P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943).

cool over a period of 15 min., except for one of the 0.85 ZnF_2:0.15 MnF_2 samples which was quenched.

It is seen that all samples except 0.75 ZnF_2:0.25 MnF_2 obey the Curie law, indicating that in these cases there is negligible exchange demagnetization. Differences in time of firing or methods of cooling have no detectable effect on the Weiss constant. If one attempts to draw a straight line through the points obtained for 0.75 ZnF_2:0.25 MnF_2 it is seen that the Curie law is not obeyed. Upon calculation of the Weiss constant of this material using a number of different pairs of experimental points as checks, substituting in expressions of the form:
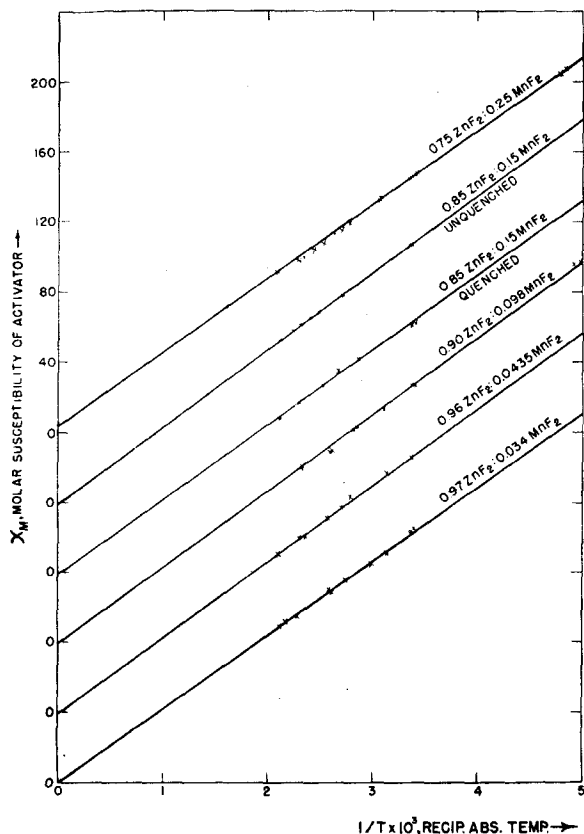
$$\chi = C/(T+\Delta),$$

TABLE I.

Sample	Obs. spec. susc. of phosphor $\chi \times 10^6$	$\chi_M \times 10^4$ for activator
0.995 ZnF_2:0.00505 MnF_2	0.40	163
0.98 ZnF_2:0.0194 Mn	2.60	159
0.957 ZnF_2:0.0435 Mn	6.34	158
0.902 ZnF_2:0.098 Mn	13.2	146
0.976 ZnF_2:0.0335 Mn	4.20	140*
ZnF_2	−0.40	
MnF_2 theoretical		147

* Different heat treatment.

distribution detectable by conventional magnetic and x-ray measurements.

CONCENTRATION DEPENDENCE OF MAGNETIC SUSCEPTIBILITY

In order to determine whether the previously observed specific susceptibilities of manganese-activated zinc fluoride are characteristic of the phosphor, a more extensive study of the precise room temperature susceptibilities was undertaken.

The experimental procedure for the determination of the mass susceptibility was a modification of the Faraday method used previously.[1] The method of analysis of the manganese content of the phosphors consists in the oxidation of the manganese to permanganate with periodate and colorimetric comparison of the resulting solution with standards in the Evelyn photoelectric colorimeter. The mean error of an analysis is about one percent.

Table I shows for 20°C the results of the measurements. The combined errors of analysis, standardization, and measurement of the susceptibilities involved in calculation of the molar susceptibility of the activator give a probable error of about two percent for the values in the last column. The molar susceptibilities tabulated are calculated using the susceptibility of the host lattice, the susceptibility of the phosphor, and assuming the additivity of the susceptibilities of the components.

The third, fourth, and fifth phosphors are the same as those on which the data for the bottom three curves in Fig. 1 were obtained. The phosphor with high activator concentration has nearly the theoretical value of susceptibility. Also a sample of the same material which had been quenched had precisely the same susceptibility. The 0.97 ZnF_2:0.034 MnF_2, which was prepared by the same method as the phosphor previously reported as having a lowered susceptibility, again shows a lower than theoretical paramagnetic susceptibility. Chemical tests similar to those of Kroger,[3] Haayman, and Bol fail to show any manganese in higher than the divalent state, which could account for the effect in this phosphor. However, the phosphor reduces both chlorine water and potassium permanganate solution to an extent corresponding to the oxidation of approximately 10^{15}

FIG. 1. Temperature dependence of susceptibilities of ZnF_2:Mn phosphors.

it is found that the Weiss constant is $+7\pm2$. By considering the Weiss constant proportional to the number of interactions per mole phosphor, the 25 mole percent phosphor is calculated to have a Weiss constant in qualitative agreement with the observed value. For phosphors containing 15 mole percent or less of activator, Debye-Sherrer x-ray data indicate only one phase and agreement with Vegard's rule, as would be expected for a random distribution of activators over cation sites.

These results demonstrate the absence of measurable magnetic interaction in phosphors of usual activator concentration and a lack of a departure from the random

[3] F. A. Kroger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York, 1948).

atoms of a divalent metal per cc of phosphor. It is likely that there is this quantity of metallic zinc atoms in the lattice and that the valence electrons of this metallic zinc become paired with the unpaired $3d$ electrons of the activator with a corresponding lowering of susceptibility. This mechanism can account for the lowering quantitatively.

It will be noticed that at low activator concentrations, the susceptibility of the activator appears to be higher than the theoretical value. There are several possible considerations which might contribute to the observed effect. One possibility is that the diamagnetic susceptibility of the lattice is reduced by the condition of local compression arising from the presence of the activator. The maximum reduction possible by this mechanism is only a small fraction of the 25 percent decrease in susceptibility of the host lattice which must be postulated to explain the observed data. Another possibility is that the introduction of activator causes the generation of a feeble paramagnetism due to incomplete quenching of the high frequency elements of the orbital moments of neighboring ions of the host lattice. It is likely that the observed high paramagnetic susceptibility is due to some effect such as this rather than to the generation of a new paramagnetic species such as Zn^+.

LUMINESCENCE EFFICIENCY *VERSUS* ACTIVATOR CONCENTRATION

On the basis of the conclusion that there is no departure from the random distribution of activator in ZnF_2:Mn, it is possible to develop from theoretical considerations an expression relating luminescent efficiency to activator concentration. The efficiency, η, is equal to the ratio of the probability of capture of an exciting photon by activators capable of emission to the total probability of capture by any component of the phosphor. For the present formulation it is assumed that (1) the emission is not absorbed; (2) the activators which are adjacent to each other are not capable of emission; and that (3) the non-adjacent activators are 100 percent efficient. σ, σ', and σ'' are defined as the capture cross sections of the host lattice, activators capable of emission, and activators incapable of emission, respectively. If C is the mole fraction of all activators in the phosphor and z is the number of nearest neighbor cation sites, it is obvious that the mole fraction of non-adjacent activators is $C(1-C)^z$. Similarly the mole fraction of adjacent activators is $C[1-(1-C)^z]$ and that of the host lattice is $(1-C)$.

Recognizing that the probability of capture by any one of the three species present is proportional to the mole fraction multiplied by the capture cross section, the following expression is readily deduced:

$$\eta = P_{\text{capture for emission}}/P_{\text{total capture}} \quad (1)$$

or:

$$\eta = \frac{C(1-C)^z\sigma'}{(1-C)\sigma + C(1-C)^z\sigma' + C[1-(1-C)^z]\sigma''}. \quad (2)$$

The same expression may be derived by considering the exponential attenuation of the excitation on passage through the phosphor and by recognizing that the capture cross sections and the concentrations of the various components are independent of the depth to which the excitation penetrates. The modifications which apply in case any one of the three original assumptions are not valid are obvious. An additional term in the denominator would take care of the effect of impurities which might act as poisons.
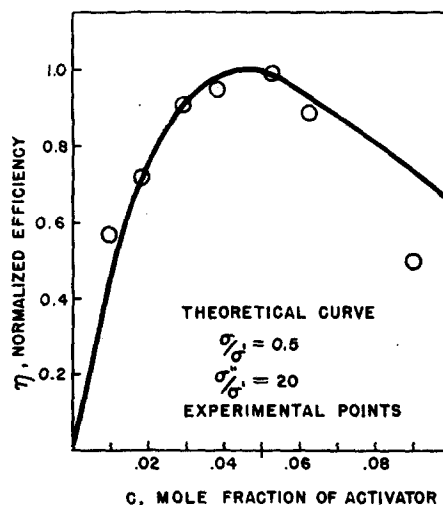
Figure 2 demonstrates satisfactory agreement be-

FIG. 2. Dependence of luminescence efficiency of ZnF_2:Mn on manganese concentration.

tween the experimental efficiencies of a series of ZnF_2:Mn phosphors at 25°C for 1849A excitation and the theoretical expression (2) using reasonable ratios of capture cross sections. The cross sections are, of course, dependent on temperature and wave-length of excitation. At the higher activator concentration the theoretical efficiency is greater than the experimental because the same cross section is used for dimer, trimer, tetramer, etc. activator ions. A more precise treatment would involve increasing capture cross sections for larger activator aggregates whose mole activator fractions are given by the successive terms of the expansion:

$$[(1-C)+C]^z = (1-C)^z + z(1-C)^{z-1}C$$
$$+ [z(z-1)/2!](1-C)^{z-2}C^2 + \cdots. \quad (3)$$

Further study of the dependence of luminescence efficiency on activator concentration for other phosphors is in progress. For sulfide phosphors it is expected that next-nearest cation sites are important because of the large activator orbitals and that σ/σ' is small so that the maximum efficiency occurs at very low activator concentrations and the absolute efficiency is quite high.

CONCLUSIONS

From measurements of the temperature dependence of specific magnetic susceptibilities of a series of

manganese-activated zinc fluoride phosphors, it is concluded that there is negligible exchange demagnetization of adjacent paramagnetic activator ions and therefore that the manganese ions are distributed at random over the cation sites. Using this distribution and recognizing that only manganese ions not having other manganese ions at any of the nearest cation sites are capable of luminescence, the dependence of luminescence efficiency on activator concentration has been successfully computed.

Infra-Red and Raman Spectra of Fluorinated Ethylenes. I.
1,1-Difluoroethylene*

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The infra-red absorption of $CF_2:CH_2$ gas has been investigated between 2 and 22.7μ with a prism spectrometer of high resolution. The Raman spectrum of the compound in the gaseous state has been photographed with a three-prism glass spectrograph of linear dispersion 15A/mm at 4358A. The 12 fundamental vibration frequencies have been assigned and the observed spectra have been interpreted in detail.

INTRODUCTION

BECAUSE of the extreme electronegativity of the fluorine atom, fluorinated hydrocarbons have unique physical and chemical properties which make the investigation of their infra-red and Raman spectra of considerable interest. While a considerable number of workers have studied the spectra of fluorinated methanes, little work has been done on fluorinated ethylenes.

Hatcher and Yost[1] obtained the Raman spectrum of $CF_2:CCl_2$ in the liquid state. Torkington and Thompson[2] have investigated the infra-red spectra of six fluorinated ethylenes and have made partial assignments of fundamentals. Very recently Edgell and Byrd[3] have obtained the Raman spectrum of liquid $CF_2:CH_2$ and have made a complete assignment of fundamentals.

As a part of a larger project on the spectroscopic properties of fluorocarbons and fluorinated hydrocarbons, we have investigated the infra-red and Raman spectra of $CF_2:CH_2$, $CF_2:CCl_2$, perfluoroethylene, $CF_2:CFCl$, and perfluoropropene. In the present paper the results obtained with gaseous $CF_2:CH_2$ will be reported.

EXPERIMENTAL

The sample of 1,1-difluoroethylene was prepared and purified in the Jackson Laboratory of E. I. du Pont de Nemours and Company. No information was available about its purity. Although it is believed that a few very faint infra-red absorption maxima are caused by impurities, the fact that it has been possible to interpret practically all of the observed infra-red and Raman bands indicates that the purity of the sample is high.

The infra-red absorption spectrum of gaseous $CF_2:CH_2$ was measured over the range from 2 to 23.7μ by means of a prism spectrometer of high resolution.[4] The cell length was 10 cm. The entire spectrum was recorded at a pressure of 775 mm and the regions of strong absorption at several lower pressures. Through the courtesy of Dr. E. K. Plyler of the National Bureau of Standards, the region from 22 to 38μ was surveyed with a KRS-5 prism instrument.

The Raman spectrum of gaseous $CF_2:CH_2$ was photographed by means of a high speed spectrograph recently developed by the Lane-Wells Company. The dispersive system of this instrument consists of three 60° prisms, with faces 153 mm wide and 75 mm high, of extra dense flint glass. The camera consists of a correcting shell, designed by P. Swings, a spherical mirror of diameter 200 mm and radius of curvature 737 mm, and a curved film holder designed so as to obstruct only ten percent of the light. A narrow mask was added, so as to prevent the 4358A mercury light from striking the film. The linear dispersion is 15A/mm near 4358A and 34 A/mm at 5000A. The entire spectrograph is enclosed in a thermostat.

The irradiation apparatus employs two high current low pressure mercury lamps with internally water-cooled electrodes of the kind developed by Welsh and Crawford at the University of Toronto.[5] The lamps, which operate on 110 volts d.c. and draw 15 amperes each, are folded, so as to have two effective straight

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[1] J. B. Hatcher and D. M. Yost, J. Chem. Phys. **5**, 992 (1937).

[2] P. Torkington and H. W. Thompson, Trans. Faraday Soc. **41**, 236 (1945).

[3] W. F. Edgell and W. E. Byrd, J. Chem. Phys. **17**, 740 (1949).

[4] Nielsen, Crawford, and Smith, J. Opt. Soc. Am. **37**, 296 (1947).

[5] H. L. Welsh and M. F. Crawford (private communication).