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The Optical Properties of Mn⁺² in Calcium Halophosphate Phosphors

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ABSTRACT

A study of the optical properties of Mn⁺² in commercial halophosphate phosphors has revealed that the Mn⁺² is located on four distinguishable sites: on the simple Ca(I) site, on the simple Ca(II) site, on a Ca(II) site adjacent to an antimony-oxygen pair, and on a Ca(II) site adjacent to a chlorine ion in those phosphors containing chlorine. The Mn⁺² fluorescence that results when the excitation is via energy transfer from antimony ions is primarily due to Mn⁺² situated on a Ca(I) site, with smaller components due to Mn⁺² located on the other sites observed.

During the twenty years that halophosphate phosphors have been utilized in fluorescent lamps many improvements have been made in their performance. These improvements have resulted in better maintenance, higher efficiency, and an increased selection of different spectral distributions. The technique used in improving the phosphors has been essentially trial and error guided by a sense of chemical intuition. It cannot be contested that this approach has been very successful in improving the phosphor. However, a basic understanding of many of the details of the operation of the phosphor has been lacking.

The difficulties in understanding the operation of the halophosphate phosphors have been due to the complexity of the halophosphate system. The commercial halophosphate phosphors form into the fluorapatite structure which has the hexagonal space group P6₃/m(C_{6h}²). This is a complicated crystal structure with 42 atoms in the unit cell. In pure calcium fluorophosphate there are two molecules of Ca₅(PO₄)₃F per unit cell, with two inequivalent sites for the Ca⁺² ions. The Ca(I) site has C₃ point group symmetry with each calcium ion having six oxygen nearest neighbors which form a twisted triangular prism about it. The Ca(II) site has C_{1h} point group symmetry. The Ca⁺² ions on Ca(II) sites are situated at the corners of equilateral triangles with an F⁻ ion in the center. In "cool white" (CW), a typical commercial halophosphate phosphor, various additives are introduced which complicate matters even further. A CW phosphor may be viewed as being calcium fluorophosphate with about 10% of the fluorine ions replaced by chlorine, 2% of the calcium ions by manganese, and an additional 1% by cadmium. Antimony is believed to be incorporated as an antimony-oxygen pair replacing a calcium(II) ion and its adjoining fluorine ion (1-3). If this model is correct, an additional ½% of the calcium ions are replaced with antimony and an additional 2½% of the fluorine ions by oxygen.

In the operation of this phosphor in a fluorescent lamp the antimony absorbs the ultraviolet radiation present in the mercury discharge. The antimony either

fluoresces in the blue region of the visible spectrum or transfers energy to the manganese ions. The manganese ions then fluoresce in the yellow. These gross features of the operation of the phosphor have been known for a long time. There have remained many mysteries, however, such as the mechanisms by which various phosphor additives cause wavelength shifts in the manganese fluorescence. For example, the incorporation of chlorine into calcium fluorophosphate shifts the manganese fluorescence emission to longer wavelengths (4). Several explanations have been proposed to explain this shift. Butler and Jerome (5) suggested that in halophosphate phosphors the manganese is located on the calcium(II) site which is adjacent to the halogens. Replacing some fluorines with chlorine might therefore shift the manganese fluorescence. Nagy, Wollentin, and Lui (6) ascribed the shift to a lattice distortion due to chlorine since the ionic size of chlorine is larger than the fluorine it replaces. Johnson (7) proposed that the manganese emission shift with addition of chlorine is due to a shift in preferred location of manganese from the calcium(I) position in pure fluorapatite to calcium(II) in the chloro-fluorapatite. There has been no way to choose between models such as these since no information on the precise locations and environments of manganese in halophosphate phosphors was available. This information could not be obtained because, in addition to the complicated apatite structure and the incorporation of relatively large amounts of antimony, manganese, cadmium, and chlorine, only powders were available for study.

After Johnson (8) succeeded in growing single crystals of calcium fluorophosphate it became possible to perform electron spin resonance measurements of the Mn⁺² to compare with the optical properties of the Mn⁺². One could therefore identify specific environmental symmetries for Mn⁺². These could then be correlated with the optical spectra of Mn⁺² at the various sites in the crystals. In a previous paper (9) we found that in fluorapatite, manganese is associated with at least four inequivalent environments; the Ca(I) site, the Ca(II) site, and two similar to the (I) and (II) sites but with "modified" environments. We labeled

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Key words: luminescence sites, energy transfer, excitation spectra.

Table I. Composition of samples

Sample	Wt % Mn	Wt % Sb	Wt % Cl	Wt % Cd	Mn(I)/ Σ Mn	Mn(II)/ Σ Mn	Mn(Sb)/ Σ Mn	Mn(Cl)/ Σ Mn
"10% Mn" FAP	1.95	0	0	0	0.63	<0.37	0	0
"Yellow halo"	1.67	0.87	<0.05	1.15	>0.8	<0.2	<0.05	0
"Cool white"	0.75	0.63	0.59	0.99	>0.6	<0.1	<0.05	~0.25

these sites the Mn(I), Mn(II), Mn(Im), and Mn(IIm). The Mn(I), Mn(II), and Mn(IIm) all possessed different optical properties that could be distinguished readily from one another by means of their characteristic excitation and fluorescence spectra, and decay times.

In this work we have used the techniques and results of our single-crystal experiments as a guide to understanding the sites of manganese and their related optical properties in the more complicated system of the real phosphor. We find this approach to be very successful in explaining many of the phenomena of manganese in commercial halophosphate phosphors.

Samples

While many different types of halophosphate phosphors were studied, three particular samples illustrated all of the phenomena observed and form the nucleus of this paper. The first is a single crystal of calcium fluorophosphate, fluorapatite, doped with manganese by pulling from a melt containing 10% manganese. The optical properties of this crystal have been previously reported (9). The other two samples are commercial phosphors, a "yellow halo" (YH) and a "cool white" (CW), produced by the Westinghouse Lamp Division at Bloomfield, New Jersey. They were prepared by firing raw mixes of luminescent grade calcium dibasic phosphate, calcium carbonate, calcium fluoride, ammonium chloride, cadmium carbonate, antimony trioxide, and manganous carbonate in an atmosphere of nitrogen. The YH was fired at 1130°C and the CW at 1180°C. The principal differences between YH and CW are that the former contains no chlorine and has a higher manganese concentration than CW. Analyses were done by x-ray fluorescence spectroscopy using a Norelco x-ray fluorescence spectrometer. The tungsten target x-ray tube was powered at 50 kV-20 mA. For manganese, a vacuum was pulled in the sample and dispersing chambers to increase sensitivity. For chlorine determinations, a PET crystal and flow counter were used to disperse and detect the radiation. Chemical analyses of the samples are listed in Table I.

Experimental Techniques

The optical excitation and fluorescence measurements were performed at 1.8°K with the samples immersed in liquid helium below the λ point to eliminate bubbling. The optical excitation and fluorescence envelopes were narrowed slightly at 1.8°K compared to 300°K. This made it easier to separate the contributions to the excitation and fluorescence spectra from the various types of Mn^{+2} present in the samples. Measurements performed at 77° and 300°K showed optical phenomena similar to those occurring at 1.8°K so that the conclusions we arrive at concerning the behavior of Mn^{+2} in our samples at 1.8°K apply to 77° and 300°K as well.

The powder phosphor samples presented an unusually difficult problem in measurement technique, particularly in the measurement of their excitation spectra. In measuring the excitation spectra of powders the strong diffuse reflectance of the excitation light into the fluorescence detector requires good rejection of the excitation wavelengths by the detector. Since the absorption of Mn^{+2} is due to a forbidden transition with an oscillator strength of less than 10^{-6} in calcium fluorophosphate (9), the ratio of excitation light intensity to fluorescence intensity was much higher than one commonly attempts to measure in powders. In addition, due to the presence of several types of manganese centers, we found it necessary at times to excite and

view at the same, or nearly the same wavelength. This required a discrimination of the excitation light compared to the fluorescence light that could only be achieved by utilizing time resolved spectroscopy and sampling only the slowly decaying after-glow of the Mn^{+2} ions ($\tau \sim 8$ msec for all species) and not the excitation light.

Our time resolved spectra were obtained by using synchronous mechanical choppers for exciting and viewing. A block diagram of the system we developed is shown on Fig. 1. Here the coupling between the reference chopper and the synchronous chopper is electrical rather than the conventional mechanical coupling. This allows a greater flexibility in the arrangement of components. Under our experimental conditions this arrangement allowed no detectable excitation light to reach the fluorescence detector. This apparatus was used to obtain both the fluorescence and excitation spectra reported here.

The precise identification of the wavelengths of several of the sharp excitation peaks shown on the figures (such as the peaks at 4009 and 4037Å) was obtained by scanning a narrow wavelength range about these peaks at a much higher resolution than was used for obtaining the figures.

Optical Properties of Mn^{+2} in a Commercial "Yellow Halo" (YH) Phosphor

While we have studied the optical properties of manganese in a wide selection of commercial halophosphate phosphors two particular phosphors, the "YH" and the "CW," illustrate all of the phenomena observed. The major difference between the YH and CW phosphors is that the YH contains no chlorine and therefore is a somewhat simpler system to study, even though YH contains more manganese than CW.

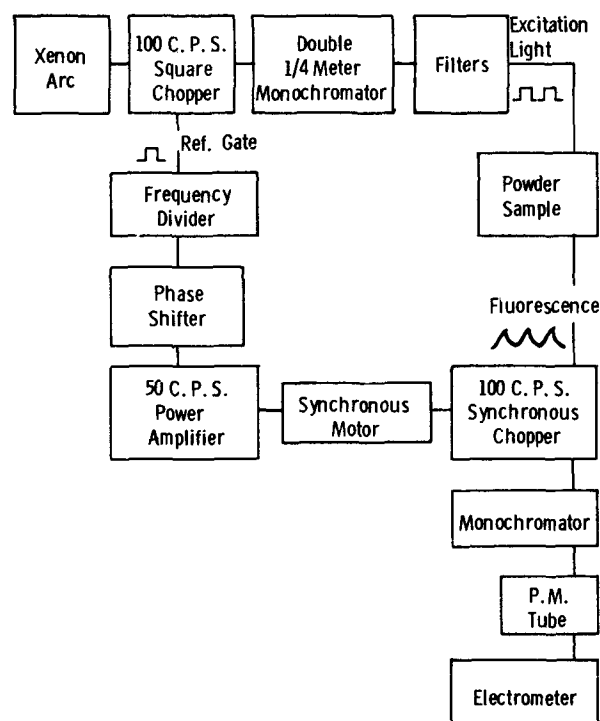


Fig. 1. Experimental arrangement for measuring the time resolved excitation and fluorescence spectra.

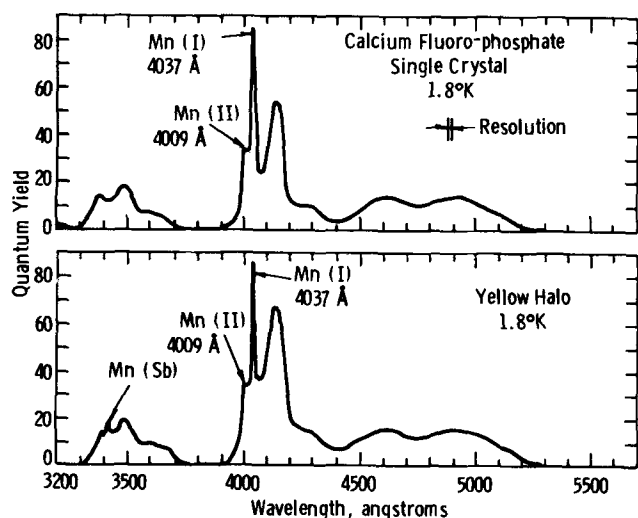


Fig. 2. 1.8°K excitation spectra of a calcium fluorophosphate single crystal and a "yellow-halo" phosphor.

Figure 2 shows the excitation spectrum of Mn^{2+} in YH along with the unpolarized excitation spectrum of Mn^{2+} in a single crystal of calcium fluorophosphate to which it is compared. In the calcium fluorophosphate crystal all of the resolved peaks shown are due to Mn(I) except for the peak at 4009 Å which is due to Mn(II). The remainder of the Mn(II) excitation lines are lost in the Mn(I) envelopes. To obtain these excitation spectra all slowly decaying luminescence (in the order of milliseconds) emitted between 5000 and 8000 Å was monitored. This wavelength range contains the fluorescences of all of the various Mn^{2+} types present in these samples. The Mn(I) and Mn(II) identifications are based on our previous single-crystal work (9). This crystal contains a concentration of 1.95 w/o (weight per cent) manganese which is in the same range of concentration as the phosphors measured which contained 1.67 and 0.75 w/o for the YH and CW phosphors, respectively. It is therefore considered to be a good crystal for comparing excitation and fluorescence spectra with the phosphors as the line widths due to concentration broadening would be similar.

The YH phosphor contains cadmium and antimony in addition to the manganese that the calcium fluorophosphate crystal contains. It can be seen that the crystal and YH possess essentially identical excitation spectra, the only difference being the appearance of a new minor excitation peak near 3425 Å which has been labeled Mn(Sb). The Mn^{2+} in the YH phosphor is therefore behaving almost exactly like the Mn^{2+} in the crystal. In analogy to the crystal we therefore come to the following conclusions about the sites of Mn^{2+} in YH: most of the Mn^{2+} is situated on the Mn(I) site, with a small contribution on the Mn(II) site. An additional Mn^{2+} center is observed in a relatively small amount, Mn(Sb), which is associated with the presence of antimony in the phosphor. We term this center the "antimony associated" manganese center. It is not due to the presence of cadmium as we have prepared YH phosphors without cadmium that still show the presence of this center. We feel that it is due to manganese situated on a Mn(II) site with an antimony ion located on an adjacent Ca(II) site. Arguments supporting this assignment are presented later in the paper. An estimate of the relative occurrence of the various Mn^{2+} species in YH is given in Table I. In our previous single-crystal work such estimates were obtained from electron spin resonance measurements. Electron spin resonance measurements were of little value in studying the Mn^{2+} in our powders since at these high manganese concentrations the resonance lines are very broad (10). The powder estimates were

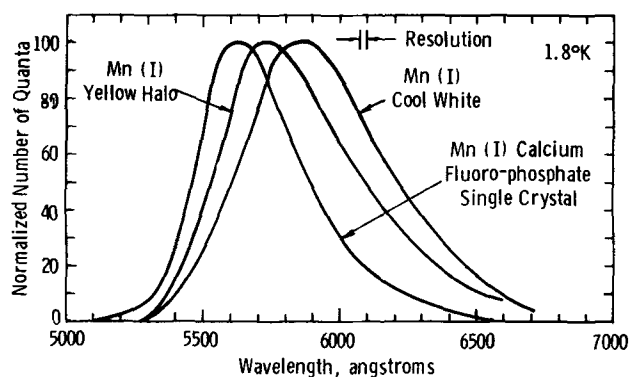


Fig. 3. 1.8°K fluorescence envelopes of the Mn(I) center in a calcium fluorophosphate single crystal, a "yellow halo," and a "cool white" phosphor.

therefore obtained by a comparison of the relative strengths of the excitation peaks of the various species of Mn^{2+} in our powders with the relative strengths of the excitation peaks of the various species of Mn^{2+} in single crystals of calcium fluorophosphate on which electron spin resonance measurements had been made. The assumptions must be made that all species have identical quantum efficiencies and that the oscillator strength of a given Mn^{2+} center in the fluorapatite crystals is the same as the comparable Mn^{2+} center in the phosphor. These assumptions introduce some uncertainty in the relative occurrence numbers stated in Table I for the powders.

The fluorescence envelopes of the Mn(I) centers in the calcium fluorophosphate crystal and the YH phosphor are shown in Fig. 3. They were obtained by pumping at 4037 Å where only the Mn(I) species is strongly excited (9). The addition of cadmium and antimony to calcium fluorophosphate has shifted the 1.8°K Mn(I) fluorescence envelope about 100 Å to longer wavelengths (the shift at 300°K is somewhat less). The Mn(Sb) fluorescence envelope was too weak to measure accurately, although it was determined that it fluoresces with an envelope that is shifted slightly to longer wavelengths than the Mn(I) envelope.

Optical Properties of Mn^{2+} in a Commercial CW Phosphor

Commercial CW phosphors contain chlorine in addition to all of the additives present in the YH phosphor. The presence of the chlorine (which represents about 10% of the total halogens) is found to create a new Mn^{2+} center associated with the presence of chlorine which we term the Mn(Cl) center. Its excitation spectrum is shown on Fig. 4 and its fluorescence envelope on Fig. 5. This fluorescence was obtained by exciting at 5450 Å which pumps Mn(Cl) but not the other manganese types. The CW phosphor contains four easily identifiable types of Mn^{2+} centers. As they result in somewhat different fluorescence envelopes it is possible to accentuate the excitation spectra of the various centers by selectively viewing at certain fluorescence wavelengths. In Fig. 4 two excitation spectra are shown. The first excitation spectrum is that which results when viewing the fluorescence occurring at 5500 Å. Viewing at 5500 Å accentuates the Mn(I) and Mn(II) excitation peaks and so this excitation spectrum selectively displays the Mn(I) and Mn(II) components. It may be seen that this excitation spectrum is identical to that observed in the fluorapatite crystal in Fig. 2. The second excitation spectrum of Fig. 4 was obtained by viewing the fluorescence occurring at 6000 Å which accentuates the Mn(Cl) and Mn(Sb) components. Some Mn(I) component is still visible, however, as there is still a sizable 6000 Å component to the Mn(I) fluorescence.

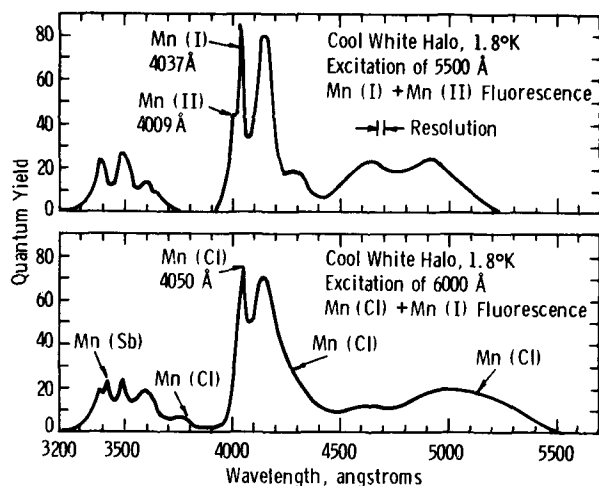


Fig. 4. 1.8°K excitation spectra of the Mn(I), Mn(II), Mn(Cl), and Mn(Sb) centers in a "cool white" phosphor.

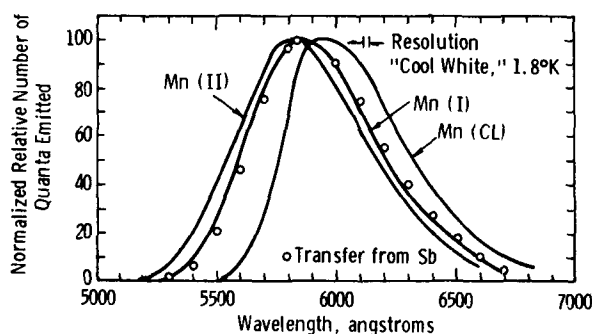


Fig. 5. 1.8°K fluorescence envelopes of the Mn(I), Mn(II), and Mn(Cl) centers in a "cool white" phosphor along with the Mn^{+2} fluorescence envelope that results when the excitation is due to transfer from antimony ions.

On Fig. 5 the normalized fluorescence envelopes of the Mn(I), Mn(II), and Mn(Cl) centers in CW are shown along with the fluorescence envelope that results when the antimony ions are pumped by 2537Å radiation and the Mn^{+2} is excited by energy transfer from the antimony. From Fig. 5 it is seen that the Mn^{+2} fluorescence envelope that results when energy is transferred from the antimony ions may be made up by a suitable combination of the various Mn^{+2} types present in the CW phosphor. On Fig. 6 we present the linear combination of the three major Mn^{+2} components that yields a composite envelope giving a "best fit" to the envelope resulting when excitation is via antimony. It occurs for approximately 70% Mn(I), 20% Mn, and 10% Mn(II). These component percentages lie within the probable error limits of the relative absorption (excitation) strengths of the various species. This implies that the various Mn^{+2} types receive relative amounts of energy from the antimony ions that do not differ greatly from their relative absorption strengths during excitation by external light. All three species therefore are active in the functioning of the CW phosphor in a fluorescent light and contribute to its composite manganese fluorescence envelope.

Discussion

The assignment of components in the optical spectra of our phosphor samples to Mn(I) and Mn(II) was relatively simple, as the Mn(I) and Mn(II) excitation and fluorescence spectra in the phosphors closely resembled their counterparts in single crystals of calcium fluorophosphate. No Mn(Sb) or Mn(Cl) centers were present in the calcium fluorophosphate crystals that we studied previously so that models for these

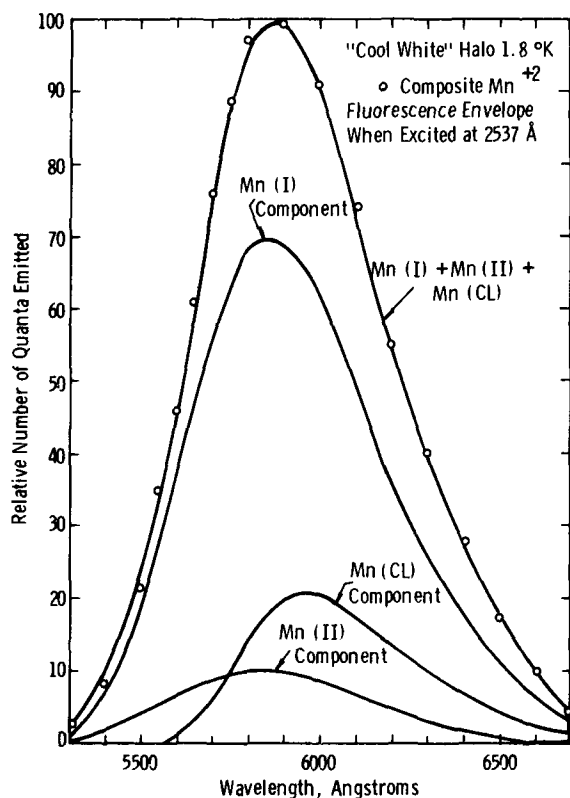


Fig. 6. Linear combination of the Mn(I), Mn(II), and Mn(Cl) centers that gives a best fit to the composite Mn^{+2} envelope that results when the excitation is due to transfer from antimony ions at 1.8°K. The combination is 70% Mn(I), 20% Mn(Cl), and 10% Mn(II).

centers must be derived from more indirect arguments. The models that we propose for these two centers are therefore somewhat speculative and represent what we believe the centers to look like, rather than what we can prove them to be.

In our previous single-crystal work we found that if our crystals were grown under certain conditions (a deficiency of fluorine and/or an excess of oxygen), defect centers would be formed along the halogen chains (9). These centers consisted of clusters of fluorine vacancies and oxygen ions substitutional for fluorine. They exhibited an attractive force on substitutional manganese ions which caused nonrandom pairing, forming centers such as the one we termed the Mn(II) "modified," or Mn(II_m) center. Our model for this center is that it consists of a manganese ion located on a Ca(II) site immediately adjacent to an oxygen vacancy complex. No corresponding center due to pairing of manganese ions located on Ca(I) sites with the defect centers was observed to occur. This is undoubtedly because the Ca(I) site is much farther away from the halogen chain than the Ca(II) site, and that an attractive force between the manganese ions and the defect centers would cause them to be located as closely together as possible, *i.e.*, with the Mn on the Ca(II) site.

Another observation we can make from the single-crystal data is that the Mn(I) and Mn(II) centers exhibit no observable modifications in their ESR or optical spectra due to the presence of the defects on the fluorine chains. Thus it appears that the excitation spectra of manganese ions are practically unaffected by the presence of defects unless they occur at a nearest neighbor position. We are therefore led to expect that the Mn(Cl) and Mn(Sb) centers, which exhibit characteristic excitation spectra that differ significantly from the Mn(I) and Mn(II) spectra, are formed by having a manganese ion located adjacent to the

chlorine ions and the antimony-oxygen complexes, respectively.

Since the chlorine atoms would most probably enter the lattice substitutionally for fluorine, one expects that in the Mn(Cl) center the manganese ion is located on a Ca(II) site adjacent to a chlorine ion. The presence of a manganese-chlorine attraction analogous to that found for the Mn(II) center may be seen from the distribution of the various types of manganese that occurs in CW. In the CW phosphor about 70% of those Mn²⁺ ions located on Ca(II) sites are Mn(Cl) centers. Since only 10% of the fluorine ions are replaced by chlorine, a random distribution of manganese and chlorine would predict that only 10% of the manganese ions on Ca(II) positions would be adjacent to chlorine ions and form Mn(Cl) centers, not 70%.

Piper has reported on ESR measurements of manganese in single crystals of calcium fluorophosphate, chlorophosphate, and mixed fluorochlorophosphates that lend support to our assignment of the Mn(Cl) center to manganese on a Ca(II) position adjacent to a chlorine. In his pure fluorophosphate crystals Piper observed only Mn(I) centers and no Mn(II) centers. In mixed crystals containing small amounts of chlorine he detected, in addition to Mn(I), a single type of Mn(II) associated with the presence of chlorine in the structure. This observation is consistent with our model of the strong interaction between manganese and chlorine ions that gives rise to the formation of the Mn(Cl) center. His failure to observe the Mn(II) center in calcium fluorophosphate is consistent with our observation that at low manganese it is incorporated as Mn(I).

Strong evidence suggests that antimony ions enter the apatite structure as antimony-oxygen pairs, with the oxygen located on a halogen site and the antimony on one of the three adjacent Ca(II) positions (1-3). We conclude that the Mn(Sb) center consists of a manganese ion located on a Ca(II) site adjacent to an antimony-oxygen complex. The Mn(Sb) center is such a minor center in CW that we are unable to determine whether the number of Mn(Sb) centers is greater than a random distribution of manganese and antimony would predict or not.

The shift in the emission envelope of the Mn(I) fluorescence to longer wavelengths as cadmium, antimony, or chlorine are added to calcium fluorophosphate is probably because these ions cause dimensional changes to the fluorapatite lattice. Norita (12) has suggested that the resultant change in the crystal field strength acting on the Mn²⁺ ions due to these dimensional changes would be expected to shift the Mn²⁺ emission envelope. While this effect is certainly present we do not feel that it is primarily responsible for the emission shifts observed. We observe no corresponding shift in the excitation spectra of Mn(I) in our phosphors when cadmium, antimony, or chlorine are added: only a shift in the emission, Norita's model would predict a shift in the excitation levels also due to the change in crystal field strength, particularly the broad excitation peak which corresponds to excitation to the fluorescence state. All of the shift appears after the Mn²⁺ ions are in their excited state, although a slight shift in the lowest lying excitation envelope with additives could easily be missed as the envelope is quite broad. That is, a larger Stoke's shift occurs to the Mn²⁺ ions when the various additives are present. We thus prefer to view the functioning of the additives as "softening" the lattice and allowing larger Stoke's shifts to occur. How this can happen may be seen from the following simple model. Figure 7 shows how a Stoke's shift is commonly pictured as occurring on an energy configuration-coordinate diagram. The ground and excited states of the ion are assumed to

be parabolic, $E \sim \frac{1}{2} k Q^2$ where k is the lattice force constant, and to couple to the lattice modes with terms V_1 for the ground state and V_2 for the excited state.

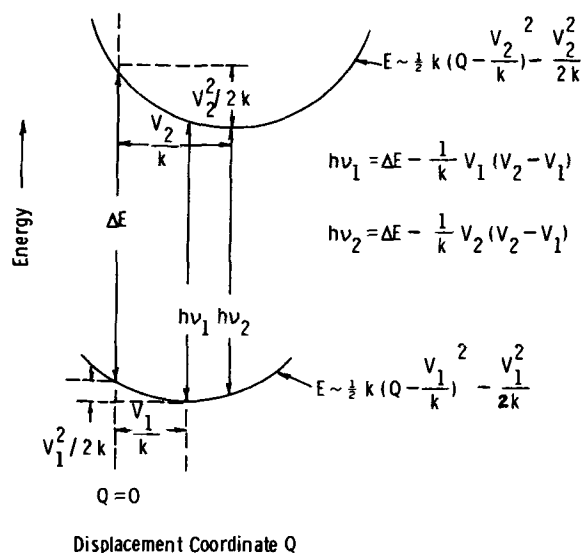


Fig. 7. Energy configuration-coordinate diagram for the Stoke's shift observed in the phosphors. The symbols are defined in the text.

The coupling to the lattice modes is assumed to yield an energy term that is linear in the lattice distortion so that coupling terms in Q^2 or higher are negligible. Adding this term to the parabolic term we have

$$E \sim \frac{1}{2} k Q^2 - QV$$

The Stoke's shift is then observed as the difference between the absorption and emission energies

absorption

$$h\nu_1 = \Delta E - \frac{1}{k} V_1 (V_2 - V_1)$$

emission

$$h\nu_2 = \Delta E - \frac{1}{k} (V_2 - V_1)^2 - \frac{1}{k} V_1 (V_2 - V_1)$$

where ΔE is the separation of the levels in the absence of coupling to the lattice modes. The difference in energy between the absorption and emission is thus the term, $\frac{1}{k} [V_2 - V_1]^2$. If k is reduced (the lattice gets softer), $h\nu_2$ shifts more than $h\nu_1$ by an amount approximately equal to

$$\left[\frac{V_2 - V_1}{k} \right]^2 \Delta k$$

where Δk is the change in the lattice force constant. If Δk is negative then the shift is toward longer wavelengths. In order for the absorption line to shift very little (the location of the center of the lowest energy excitation envelope in this case) while the emission line shifts a much greater amount, one requires that V_1 is small and that V_2/V_1 is large. It is a reasonable assumption that the excited state of the manganese ions would couple more strongly with many of the lattice modes than does the ground state. The observation of a Stoke's shift and the absence of a zero phonon line (9) already informs one that the coupling terms V_1 and V_2 are considerably different. While admittedly crude, this model does qualitatively explain the increased Stoke's shift observed as additives such as chlorine are incorporated into calcium fluorophosphate.

Conclusions

In commercial halophosphate phosphors, Mn²⁺ can find itself in four distinct environments: on the simple Ca(I) site, on the simple Ca(II) site, on a Ca(II) site

adjacent to an antimony-oxygen pair, and on a Ca(II) site adjacent to a chlorine ion in those phosphors containing chlorine. In the most commercially important phosphor of the group, CW, we find that between 60 and 70% of the manganese is present as Mn(I), between 5 and 10% as Mn(II), between 1 and 5% as Mn(Sb), and between 20 and 30% as Mn(Cl). The phosphor functions in the following manner in the fluorescent lamp. The antimony ions absorb the 2537Å radiation and either fluoresce or transfer energy to Mn^{+2} ions. Most of the Mn^{+2} fluorescence that results is due to Mn(I), with smaller components due to Mn(Cl) and Mn(II), and a very small component due to Mn(Sb). The fluorescence envelope of Mn(I) in CW is at longer wavelengths than Mn(I) in calcium fluorophosphate. This Mn(I) envelope shift is primarily responsible for the color shift observed in the CW phosphor relative to calcium fluorophosphate. The shift is not due to a redistribution between the Ca(I) and Ca(II) sites due to the introduction of Sb, Cd, and Cl as Johnson proposed (7), nor due to the formation of new Mn(Cl) centers as Butler and Jerome (5) proposed, although the formation of Mn(Cl) centers does occur to some degree and does cause a slight additional wavelength shift to the composite Mn^{+2} fluorescence envelope.

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The Effect of Rapid Cooling on Divalent Manganese Ions in Calcium Fluoro-Chlorophosphate Phosphors

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ABSTRACT

Quenching experiments were performed on manganese-activated calcium fluoro-chlorophosphate phosphors. Changes in the optical properties of the manganese ions due to quenching were studied in order to explain the manganese fluorescent envelope shift in quenched phosphors reported by other workers. We find that quenching causes a change in the nearest halogen neighbors of manganese ions located on the so-called "Ca(II)" positions. In slowly cooled phosphors these ions have mostly chlorine ions as nearest neighbors while in the quenched phosphors many of the chlorine ions are replaced with fluorine. It is shown that this redistribution will produce a shift in the manganese fluorescence envelope equal in magnitude to that experimentally observed.

Apple and Ishler (1) have observed that if chlorine-containing calcium halophosphate phosphors, activated by antimony and manganese, are cooled very rapidly (from 600°-1200°C) to room temperature, that the spectral distribution of the manganese fluorescent emission shifts to slightly shorter wavelengths while the antimony emission is unchanged. This effect was found to be reversible upon annealing and did not occur in calcium fluorophosphate. They proposed two alternative models to explain this effect. One explanation involved a redistribution of manganese among the various sites it may occupy in these phosphors, due to the quenching. Since one would expect somewhat different emission wavelengths for manganese located on

different sites a shift in the composite emission envelope could result from such a redistribution.

Their second model involved changes in the location of the chlorine atoms in the crystal structure of the phosphors due to quenching. It was proposed that a rapid cooling could freeze the chlorine atoms into a more random arrangement than the equilibrium configuration at low temperatures.

At the time they published their paper, progress in understanding the structural and optical properties of the calcium halophosphate phosphors had not yet reached the point where these models could be tested. Since then, some progress has been achieved in characterizing the structural modifications that exist, the nature of the sites that manganese ions occupy in the calcium halophosphate phosphors, and the optical properties of the manganese ions on those sites. This

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Key words: quenching, luminescence, fluorescence, optical properties, centers.