Comparison of the observed shifts with Tinkham's results is rather more indirect than for MnF_2 because the presence of induced dipoles (which give rise to temperature-independent terms in the susceptibility) makes the net spin component $\bar{S}$ in any direction no longer proportional to the susceptibility. This effect is probably not too serious in FeF_2, where Tinkham indicates that the only low-lying levels are the five spin states ($S=2$). These have an over-all splitting of about 50°K, and it should be a reasonable approximation at our temperatures to assume that the susceptibility and $\bar{S}$ are proportional to one another. Tinkham measures only A_z^{I} and A_z^{II} but the other values can be estimated using Tinkham's Eq. (II, 9) and the values for A_σ and A_π he gives for MnF_2. This gives

	x	y	z	
A^{I}	23	24	25	$\times 10^{-4}$ cm^{-1}.
A^{II}	22	18	16	

Nirra and Oguchi[8] interpreted the susceptibility in undiluted FeF_2 using $g_{\parallel}=2.45$ and $g_{\perp}=2.24$. If these values are used instead of Tinkham's, all values of α and $\Delta\alpha$ are reduced by about 9%.

In common with the MnF_2 values, the predicted shifts are a few percent larger than the observed shifts. This is probably due to the fact that in these salts the separation of the fluorine from its neighboring paramagnetic ion is about 5% greater than it is in ZnF_2, so that the s-electron overlap, and hence the values of A^N, are expected to be smaller. Both salts have a much larger $\Delta\alpha$ than is predicted. This could be due to the fact that the distance to the nearest fluorine neighbors I changes less than that to the fluorine neighbors II so that an increase in the ratio $A^{\text{I}}/A^{\text{II}}$ may occur leading to an increased anisotropy.

In the case of CoF_2 the assumption that $\bar{S}$ is proportional to the susceptibility is probably a very poor one, especially as the specific heat data of Stout and Catalano[5] suggest that another doublet state lies some 240°K above the ground doublet. Also it is difficult to know what g values to use as Tinkham[3] and Nakamura and Taketa[9] give widely differing results. Tinkham's g values, measured in a diluted salt, differ greatly from 2, and he explains these values by assuming a ground state with large admixtures of several free ion states. Nakamura and Taketa estimate their g values by fitting the susceptibility of the concentrated salt theoretically on the assumption that the ground state is an orbital singlet, with small admixtures of other states, so that their values are close to 2. This theory would require considerable modification to fit the diluted salt. Values of α have been calculated by using both sets of g values. Tinkham was unable to distinguish between the hyperfine structures of the two bonds and gives only an average $A_y=32$ and $A_z=21(\times 10^{-4}\text{ cm}^{-1})$. These suggest that A^N in terms of real spin is isotropic ($A^N=14\times 10^{-4}\text{ cm}^{-1}$) and hence one can estimate $A_x=16\times 10^{-4}\text{ cm}^{-1}$ using Tinkham's g values. The large discrepancy between the measured and calculated values of α is not unexpected since the treatment is very approximate.

In both salts the signal/noise ratio is proportional to H_1 ($\gamma^2 H_1^2 T_1 T_2' \ll 1$); and the line width, measured between points of maximum slope, is about 27 gauss and is independent of temperature. This is close to the value of 28.5 gauss given for MnF_2.

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Photoelectroluminescence with Visible Response

D. A. Cusano

General Electric Research Laboratory, Schenectady, New York

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PHOTOELECTROLUMINESCENCE[1] has been reported for the phosphor ZnS:Mn,Cl.[2] It is the purpose of this letter to report on the recent observation of this phenomenon in the luminescent materials ZnS:As,Cl and ZnS:P,Cl. In contrast to the manganese-activated phosphor, the spectral responses are much broader and extend well into the blue region of the visible spectrum. Similarly, however, the photoelectroluminescent emission intensity exceeds the intensity of the radiation incident on the phosphor. Consequently, the energy for emission originates primarily from the electric field to which the phosphor is subjected, and not from the incident radiation. The steady irradiation brings about and maintains the conditions for electroluminescence. Though the efficiency of the electroluminescence is still rather low, the improvement in spectral response and the increased energy gains make these phosphors of interest from the standpoint of solid-state light amplification.

The phosphors are formed as thin, continuous layers by the vapor reaction method.[3] The electrodes for application of voltage consist of a transparent TiO_2 coating on one side and a metallic film on the other. The dotted curves of Fig. 1 compare the arsenic and

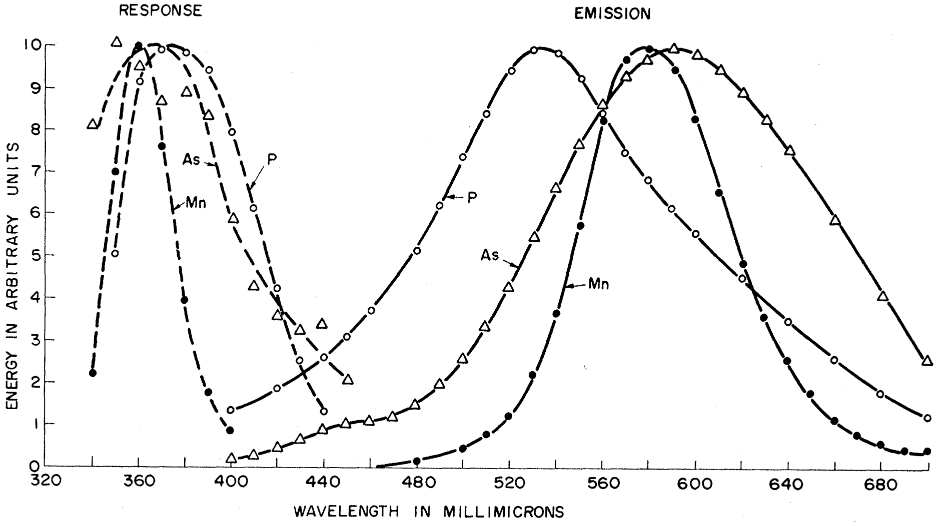

Fig. 1. The response and emission spectra of the present photoelectroluminescent phosphors.

phosphorus spectral responses to that of a manganese-activated film. The data were taken by maintaining 100 volts dc across 10-μ samples of each screen and measuring the light output during monochromatic irradiation. Corrections were made for the photomultiplier response and the incident intensity from the monochromator so that the data represent constant energy irradiation. The response bands of arsenic and phosphorus, though peaking in the near ultraviolet, are seen to be twice as broad as that of manganese, exhibiting about one-half of their peak values around 4100 A. The solid curves of Fig. 1 compare the emission spectra of these same phosphors.

The dependence of photoelectroluminescent output on incident 3650 A intensity is shown in Fig. 2 for a typical ZnS :As,Cl sample. Radiant-energy gain extends from about 0.04 to 40 microwatts/cm^2 input. The amplification ratios would be half as great if 3650 A were replaced by 4100 A. The fact that the variation of the output is less rapid than linear indicates that image contrast deteriorates during the intensification process. The photoelectroluminescent response times decrease with incident intensity and are comparable to those reported for the manganese-activated phosphor.

These results can be explained by the interpretation proposed for the photoelectroluminescence of ZnS :Mn,Cl:[1] (1) the absorption of incident radiation releases charge carriers and leads to an increase in electric field in the region of the negative electrode, (2) increased injection of electrons from the cathode occurs, and (3) the acceleration of these conduction electrons in the high-field region leads to collision excitation of the

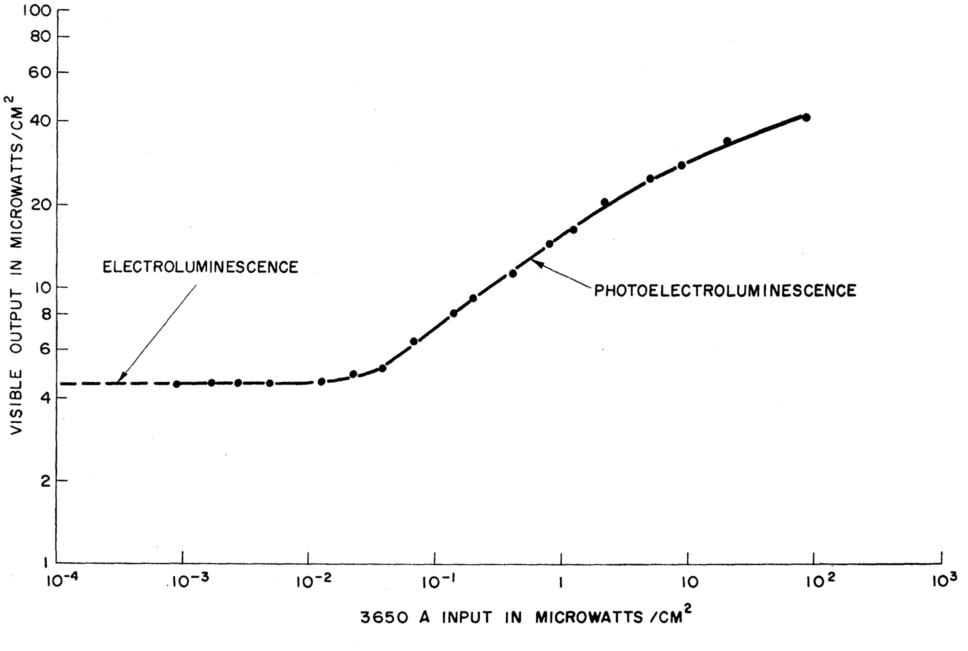

Fig. 2. The variation of photoelectroluminescence with incident intensity for a ZnS :As,Cl film.

activator centers. This mechanism requires that the excited centers responsible for emission be stable in a high field. The stability of the manganese center is well known, whereas the apparent stability of the arsenic and phosphorus centers is unexpected.

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Shift of Center Frequency of an Ammonia Inversion Spectrum*

I. Takahashi, T. Ogawa, M. Yamano, and A. Hirai
Department of Physics, Faculty of Science, Kyoto University, Kyoto, Japan

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THE authors have found that the frequency of the Stark modulation atomic clock[1] can shift depending upon the ammonia pressure of the Stark cell and within a certain time interval after the gas was introduced into the cell.

The frequencies of the clock have been plotted *versus* the squares of Stark electric field for various states of the gas and the curves have all become very nearly parallel straight lines. From this fact, the above frequency shift can be ascribed to the shift of the center frequency of the $J=3$, $K=3$ inversion transition of ammonia, though the latter had been considered negligible at sufficiently low pressure in earlier work.[2-6]

In order to measure the frequency shift, the ammonia gas was prepared in two different states of which one (wet) was saturated with water vapor and the other (dry) free from it. The measurements were carried out by using a frequency meter of precision better than 2×10^{-9} which is employed as a frequency comparator between the ammonia inversion spectrum and the 100-kc quartz oscillator.

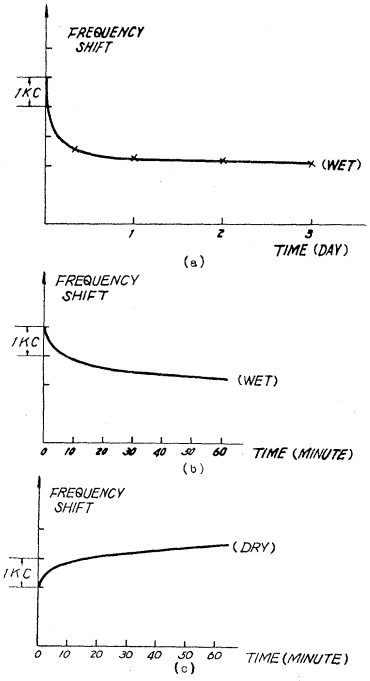

FIG. 1. Typical examples of the frequency shift, the initial frequency not being absolutely determined. (a) Long-time frequency shift of wet ammonia. (b) Continuously recorded frequency shift of wet ammonia for first hour. (c) Continuously recorded frequency shift of dry ammonia for first hour.

Figure 1 shows the shifts of the atomic clock frequency corresponding to the ammonia inversion spectrum ($J=K=3$) with the time beginning at the introduction of the gas into the cell at a pressure of 3×10^{-3} mm Hg. Figure 2 shows the pressure dependence of the frequency shift.

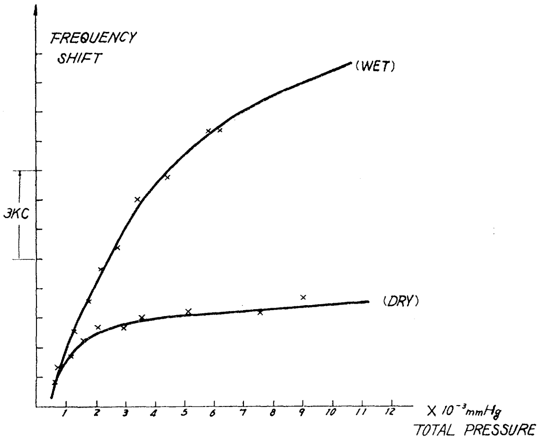

FIG. 2. Typical examples of frequency shift as a function of the total pressure. The shifts are measured at a definite time after the introduction of the gas.

The present experimental results give only qualitative information. However, two reasons for the frequency shift of the spectrum may be considered: (1) effects resulting from the adsorption of ammonia and other gas molecules contained in the cell by the wall, and (2) the interaction between ammonia molecules and foreign gas molecules.

It is planned to analyze quantitatively the sample gases at various time instants after the introduction into the cell and to measure the frequency shifts respectively when the gas is pure ammonia and when it is accompanied by foreign gases by using a Stark cell which is completely outgassed. This work is now partly in progress.

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