Paramagnetic Resonance in Phosphors at Microwave Frequencies

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THIRTY-TWO inorganic phosphors containing paramagnetic activators have been examined. The phosphors are luminescent under ultraviolet irradiation and their paramagnetic resonance spectra have been investigated both when unirradiated and irradiated. Because the mechanisms of luminescence and paramagnetism both depend upon unpaired electrons, it has been anticipated that a change in paramagnetism would occur upon excitation to luminescence. The emphasis has been placed on phosphors containing dilute concentrations of doubly ionized manganese as activator. Mn^{++} is in an S state and, in dilute concentrations, should act very nearly as an ideal paramagnetic substance.

The unirradiated spectra may be classified into five groups. The first four groups contain all the manganese activated phosphors and the fifth group contains all nonmanganese activated phosphors. The spectrum for all members of group one consists of a single broad absorption curve from 750 to 1000 gauss wide. Group two contains four phosphors each of whose spectrum consists of six clearly defined peaks interpreted as hyperfine structure. The spacings between peaks vary from 68 to 88 gauss depending upon the host crystal. Group three contains two phosphors whose complex spectra contain thirty lines attributed to a combined fine and hyperfine structure. No spectrum could be resolved for the members of group four. Likewise, the phosphors of group five yielded no resolvable spectra.

The most striking features of the Mn^{++} spectra are the isotropic hyperfine structure and the fine structure resulting from crystal field splitting. These spectra have been shown to fit, qualitatively, the theory and mechanism proposed by Abragam and Pryce while quantitative discrepancies between theory and experiment have been indicated. Arguments have been offered based upon line broadening as a function of crystal field symmetry to account for the large line widths in group one and the lack of spectra in groups four and five. The arguments fit the existence of highly resolved spectra in groups two and three. The spectroscopic splitting factor, g, of all spectra was two (the free spin value) as expected for an S state. The hyperfine spectra verify the spin of the manganese nucleus as being 5/2.

The results of investigating the irradiated spectra have been negative with the exception of indications of photoconductivity. The negative results may well arise from inadequate volume illumination of the phosphor sample. Further research into illumination techniques and cavity design may rectify the situation and provide a critical, experimental test of the anticipated change in paramagnetism.

The experimental method utilized X-band microwave equipment and static magnetic fields of the order of 3350 gauss. The unique character of the technique consists in superposing a 2–5 gauss ac magnetic field sweep upon the static field while traversing the field range of interest in approximately four minutes. At each value of static magnetic field, the ac information signal is proportional to the slope of the absorption spectrum at that value. A phase detector is used to convert the information signal into a phase and amplitude dependent signal. In this manner the sign of the slope is conserved, permitting reconstruction of the original absorption curve. The irradiation technique consists in the removal of the ac magnetic sweep and square-wave-ultraviolet illumination of the sample. The resultant signal, upon traversal of the magnetic field range, should be proportional to the difference in spectra of the unirradiated and irradiated sample.