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Letter to the Editor

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Crystal Luminescence—Paramagnetic Ions as Centers

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IN a previous communication,[1] after considering the polarization of luminescence of ruby, it was stated that a general interpretation of crystal luminescence based on the following concept could be attempted: "The absence or existence of luminescence is conditioned by the complete quenching of the orbital moment (caused by crystalline fields) of a possible center or its conservation along one or more directions within the crystal."

Among the luminescent solids which give discrete or line spectra are those in which paramagnetic ions act as centers of luminescence. Below are given some facts regarding the luminescence of this class of crystals, which support the above concept.

(1) It is now well known that the sharp-line luminescence of either pure rare-earth salts or solids containing rare earths as impurities, arises from the transitions within the shielded incomplete $4f$ shell of the rare-earth ion. The effect of this shielding from the surrounding fields is to leave the orbital moment of the ion free to orient in a magnetic field, like a paramagnetic gaseous atom. This is reflected in luminescence as the ease with which the rare-earth ions take up positions[2] as luminescent centers in any crystalline matrix. Without regard to the structure of the surrounding matrix, the ion remains a center of sharp-line luminescence, as there is no quenching of the orbital angular momentum along any direction within the crystal. There is thus no directional fixation of the L moment of the ion owing to surrounding fields.

(2) Solids activated by ions of the transition elements give discrete spectra arising from transitions owing to the rearrangement of electrons in the incomplete $3d$ shell. Trivalent Cr^{+++} and divalent Mn^{++} ions will be considered here as representatives. In the case of phosphors activated by chromium, it is found[3] that the Cr^{+++} ion acts as a luminescent center only where Cr_2O_3 can be isomorphous with the crystalline matrix in which it is embedded. The Cr^{+++} ion, which then can be shown to occupy a definite position[4] in the lattice of the matrix crystal, will have its orbital angular momentum conserved along one or more definite directions, depending on the symmetry of the surrounding fields and will then be in a condition to be excited and to luminesce. If it is embedded anyhow in a matrix, not isomorphous with Cr_2O_3, the ion, being subject to totally unsymmetrical[5] fields, will have its orbital moment completely quenched and there will be no luminescence. Conservation of the L moment along a single definite axis of symmetry of the crystal will result in polarization of luminescence, which in the case of corundum has already been referred to.[1]

Manganese, on the other hand, i.e., Mn^{++} ion, enters a wide variety of crystal matrices as an impurity and remains luminescent. Randall[6] has shown it to luminesce in pure halide crystals as well as in ZnS, $MgSO_4$, $MgSiO_3$, $Cd_2B_2O_5$, etc. The Mn^{++} ion having $3d^5\ {}^6S$ as the basic term is in the S state and has therefore little orbital interaction with the surrounding fields. There is no quenching effect caused by the fields and the ion is in a position to be excited and to luminesce within matrices of varied structures.

(3) The observations of Rupp[6] on the partial polarization of luminescent light, perpendicular to an applied magnetic field, of ZnS phosphors, activated by Mn and Cu ions, are also significant. This shows that the paramagnetic ions are comparatively free to orient in a magnetic field, the effect being greater for Mn—an ion of greater magnetic moment. Riehl[7] has shown that the activating atoms are "mobile" within the ZnS lattice and that there is sufficient space for the ion within the unoccupied tetrahedra (with S atoms at corners) the interlinking of which gives the ZnS lattice. The freedom to orient and the mobility of the ion mean that there is feeble interaction of the L moment with the crystal fields and that there is no quenching effect. This is then accompanied by luminescence.

It is seen from the above cases of crystal luminescence caused by paramagnetic ions as centers that the interaction of the orbital moment and the surrounding fields has to be considered, the existence of luminescence being conditioned by the conservation of the orbital angular momentum along one or more directions within the crystal.

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[2] Tomaschek, Trans. Faraday Soc. **35**, 148 (1939).
[3] Deutschbein, Physik. Zeits. **33**, 874 (1932).
[4] B. V. Thosar, Phil. Mag. **26**, 878 (1938).
[5] Van Vleck, *Theory of Electric and Magnetic Susceptibility* (Oxford University Press, 1932), p. 288.
[6] Rupp, Ann. d. Physik **75**, 326 (1924).
[7] Riehl, Trans. Faraday Soc. **35**, 135 (1939).