

## LETTERS TO THE EDITORS

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**The Light Emitted by Europium Compounds**

SOME time ago, my co-workers and I<sup>1</sup> found that the well-known blue fluorescence band of some fluorites is due to traces of bivalent europium. In later papers<sup>2</sup>, I showed that europium can easily be reduced to the bivalent form by heating in various basic materials.

F. Weger, in this laboratory, has studied the fluorescence spectrum of  $\text{Eu}^{++}$  in various substances. There is always a broad band in the blue, but the position of the maximum varies widely with the nature of the basic material and with the way the sample has been heated; heating on a platinum wire in the flame shifts the maximum towards longer wave-lengths as compared with a sample heated in a glass tube.

This investigation was well advanced when I saw the important paper by S. Freed and S. Katcoff<sup>3</sup> on the absorption and fluorescence spectra of bivalent europium. These authors, too, note the strong dependence of the maximum on the nature of the crystalline surroundings, and give for the bands of  $\text{Eu}^{++}$  the interpretation proposed by me<sup>4</sup> in 1936, namely, transitions between  $4f$  and  $5d$ , etc.

With a mixture of calcium chloride and borax containing traces of europium, we get by suitable heating a bright yellow fluorescence with a maximum somewhere in the near infra-red for which we have as yet no interpretation.

A borax bead with traces of europium glows, when heated on a platinum wire loop in the blow-pipe flame, with a blue light<sup>5</sup> nearly as intense as the blue component of the light emitted by the glowing platinum wire; the light resembles in colour the fluorescence excited by ultra-violet. This might be chemiluminescence (the candoluminescence of Nichols and his co-workers); but it might also be an extreme case of selective temperature radiation as, according to Freed and Katcoff, the absorption of bivalent europium is very strong in the near ultra-violet<sup>6</sup>.

A more detailed account appears in the *Wien Anzeiger* of December 2, 1948, and in the *Acta Physica Austriaca*.

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<sup>1</sup> Haberlandt, H., Karlik, B., and Przibram, K., *Wien. Ber.*, IIa, **143**, 151 (1934).

<sup>2</sup> Przibram, K., (a) *Wien. Ber.*, IIa, **144**, 141 (1935); (b) *ibid.*, **147**, 261 (1938).

<sup>3</sup> Freed, S., and Katcoff, S., *Physica*, **14**, 17 (1948).

<sup>4</sup> Przibram, K., *Z. Phys.*, **102**, 331 (1936).

<sup>5</sup> Przibram, K., *Wien. Anz.*, 98 (1946). In this paper ref. 2 ought to read: Nichols, E. L., and Boardman, L. J., *J. Opt. Soc. Amer.*, **20**, 115 (1930).

<sup>6</sup> Compare also Przibram, K., ref. 2(b).

**Formation of Microscopic Crystals on Crystal Surfaces Exposed to  $\alpha$ -Rays**

DURING some experiments on the coloration of rock salt by the  $\alpha$ -rays of polonium, we noticed that the surface exposed to the rays in air became dull. Examined under the microscope, it was found to be covered by minute birefringent crystals which could

be identified as sodium nitrate. Similar crystals are also formed on exposing rock salt to the action of nitric acid fumes or to nitrogen dioxide prepared by heating lead nitrate. The crystals obtained when exposing rock salt to  $\alpha$ -rays are evidently due to the formation of nitrogen dioxide by the rays in air. The action of the  $\alpha$ -rays on the rock salt surface seems, however, also to intervene; various samples of rock salt that show differences in the rate of colouring by the rays also show differences in the number of microscopic crystals formed, while no difference is found when nitrogen dioxide alone acts on the same samples. Sometimes the microscopic crystals show a marked orientation on the rock salt surface.

On potassium chloride, crystals of potassium nitrate are formed. On potassium bromide, however, there appear isotropic triangular crystals which cannot be potassium nitrate (birefringent), their melting point also being much higher. Such isotropic triangular crystals are also occasionally found on sodium chloride and potassium chloride; so far we have not been able to identify them.

On fluorite and on calcite we have obtained anisotropic crystals, which cannot be the known form of calcium nitrate, as this substance is isotropic.

A more detailed account of this work appears in the *Wien. Ber.* and the *Acta Physica Austriaca*. We are continuing these investigations.

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**Decoloration and the Ultramicroscopic Behaviour of Natural Blue and Violet Rock Salt**

THE absorption spectrum of blue rock salt from Stassfurt was determined photo-electrically in the natural state and after heating for a certain time at various temperatures. The spectrum shows the well-known high maximum at  $653 \text{ m}\mu$  and the smaller one at  $535 \text{ m}\mu$ . On increasing the time of heating, the first maximum begins to shift towards shorter wave-lengths; its intensity increases at first and then decreases. The second maximum does not alter its position; it decreases immediately and disappears sooner than the first. The violet salt from the Grimberg mine in the Werra valley behaves quite differently. It shows only one maximum, at  $583 \text{ m}\mu$ , which is not displaced after heating, and begins to decrease immediately.

The ultramicroscopic behaviour of the two sorts of salt is also quite different. The blue salt from Stassfurt shows the well-known bright red Tyndall cone, the violet one at the most a colourless cone not brighter than that sometimes observed in colourless rock salt. The following experiment makes the difference still more impressive: by heating, one can make the blue salt turn violet, with an absorption spectrum identical with that of the natural violet salt. But the former sample shows now a bright yellow Tyndall cone; the latter, as already mentioned, only a weak colourless one.

This seems to support the assertion made by K. Przibram<sup>1</sup> a long time ago, that there is an intermediate stage between the primary amicroscopic yellow colour ( $F$ -centres) and the colloidal blue, that is, an amicroscopic violet or blue colour, perhaps due