

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the

twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Mass of the Neutron and the Constitution of Atomic Nuclei

One of the great difficulties in the theory of atomic nuclei is to account for the difference in energy emission by the same substance during a β -disintegration. This difficulty is so great that in some circles the idea of abandoning the principle of conservation of energy in processes involving the emission or capture of nuclear electrons is taken into consideration.

J. Chadwick's discovery of the neutron suggests a solution, if we assume, that the masses of all neutrons are not identical, but assume values within a certain small range, corresponding to the limits of energy variation in β -spectra. The behavior of such neutrons in nuclei would be practically equal, until they split up in protons and electrons, which would have different energy contents from nucleus to nucleus.

If the assumption proposed is correct it would follow that if the nuclei of a given atomic species contain such neutrons their masses would also fall within a small range, or, in other words, a plot of their masses, taken by a sufficiently sensitive mass-spectrograph, against their number would not be a sharp straight line but some sort of a bell shaped curve.

It remains to be seen, what difficulties are brought into the mathematical treatment of wave and quantum mechanics by this assumption (Pauli's principle, statistics, etc.).

A. v. GROSSE

Kent Chemical Laboratory,
University of Chicago,
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Interpretation of Line Spectra in Crystals

Recently the writer received a letter from Professor Pringsheim of Berlin asking him whether the theories of O. Deutschbein and R. Tomaschek on the interpretation of the sharp line phosphorescence spectra in solids were in good agreement with the line absorption spectra of solids which are being investigated in this laboratory.

As the theories in question are attracting considerable attention it was thought wise to publish a general letter pointing out some aspects of the theories which would have to be modified in order to bring them into agreement with the absorption spectra data.

Otto Deutschbein¹ has attempted to explain the sharp line phosphorescence spectra of the chromium activated "phosphors" on the assumption that the lines originate from a ${}^4F-{}^2G$ transition. He points out that all the different phosphorescence spectra contain an intense doublet at about the same frequency and that this doublet also appears in the pure light absorption spectra of the chrome alums.²

H. E. White³ has analyzed the emission spectra of gaseous Cr^{+++} ion and has found that the 4F terms are separated from the 2G terms by about $15,000\text{ cm}^{-1}$ and as this is about the position of the doublet in the solid spectra Deutschbein concludes that the doublet arises from a transition between these states. He further assumes that the spectroscopic terms found for the gas spectra are very little changed in the solid state and he attributes the doublet specifically to either a ${}^2G_{9/2}-{}^4F_{9/2}$, ${}^2G_{7/2}-{}^4F_{7/2}$ or a ${}^2G_{9/2}-{}^4F_{7/2}$, ${}^2G_{7/2}-{}^4F_{9/2}$ transition.

While the main features of his explanation of the

phosphorescence spectra seem highly probable, this specific interpretation seems very unlikely, for several reasons.

According to his scheme the ${}^4F_{9/2}$ level lies about 950 cm^{-1} , and the ${}^4F_{7/2}$ about 550 cm^{-1} above the basic level and at -195°C the population of atoms in this state, according to the Boltzmann distribution, would be negligible. Therefore one would not expect to observe absorption lines from these states at liquid air temperatures. In the case of Sm^{+++} , where states occur at about 155 , 210 , 300 cm^{-1} above the basic level, Spedding and Bear⁴ have shown that at -195°C the lines originating from the 300 cm^{-1} levels are entirely absent and those from the 210 cm^{-1} level rapidly fade out in intensity as the temperature is still further lowered. The doublet in the case of the chrome alum is still strong at -195°C and certainly is not fading out.

Also De Hass and Gorter⁵ have investigated the magnetic susceptibility of Cr^{+++} in chrom alum from 14.3°A to 298°A and found that it did not have a Curie constant corresponding to a ${}^4F_{9/2}$ term but that the spin and orbital moments had uncoupled and that only the spin oriented, the orbital moment presumably having precessed out due to the strong electric fields of the crystal.

One would then expect the low lying levels of Cr^{+++} in

¹ O. Deutschbein, Zeits. f. Physik. **77**, 489 (1932).

² H. Sauer, Ann. d. Physik. **87**, 197 (1928).

³ H. E. White, Phys. Rev. **33**, 672 (1929).

⁴ Spedding and Bear, Phys. Rev. **42**, 58 (1932).

⁵ De Hass and Gorter, Leiden Comm. 208°.

solids to be quite different from the gas levels, since the 4F term has evidently gone over to a configuration corresponding to the "strong electric field" case. The absorption lines would then arise from the lowest levels of this group.

It might be mentioned here that if the electric fields of the neighboring atoms are not strong enough to destroy the $\Sigma l = L$, $\Sigma s = S$ coupling the distance between the centers of the ${}^4F-{}^2G$ multiplets will not be greatly changed in going over to the strong field case.

The weak companion lines of the chief doublet which he mentions in his paper are probably of the same type as the main doublet except they are weak due to a low probability of transition. Thus, for example, Spedding and Bear⁶ have found weak lines in the absorption spectra of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ which arise from the splitting of the excited levels due to the strong electric fields of the crystal. These lines are so faint, due to the low probability of the transition, that they can be observed only in extremely thick crystals.

Tomaschek⁷ has extended the theories of Deutschbein in explaining the phosphorescence spectra of the rare earths. Here, however, the "active" $4f$ electrons are shielded from the electric fields of the neighboring atoms by the completed $5s$ and $5p$ shells, and it is known from magnetic data that the $4f$ electrons couple together with Russell-Saunders coupling to give terms which resemble those found in gases. In the "active centers" which are excited by the cathode rays, there is no reason to expect the selection rules of gaseous spectra to hold so that transitions between terms arising from the $4f^n$ configurations might be expected. On the other hand, in pure light absorption spectra one would expect the selection rule forbidding transitions when Δn and Δl are zero to hold, as the electric fields of the crystal are not strong enough to break down the Russell-Saunders coupling of the $4f$ electrons. Thus, as might be expected, the close correlation between the phosphorescence spectra and the absorption spectra which exists for the chromium compounds is lacking with the rare earths.

Some correlation, however, might be expected as the transitions of the type ($4f^n-4f^{n-1}5x$) which are almost certainly found in absorption⁸ might also be observed in phosphorescence.

Lines arising from these transitions will be very sensitive to the type of crystal structure, etc. as the $5x$ electron will be outside the shielding action of the $5s$ and $5p$ shells. This electron, also due to the shielding, will be more loosely coupled to the inner $4f$ electrons so that its coupling will be jj with the resultant of the R.S. coupling of the core electrons.

In the case of compounds of Sm^{+++} (as well as Pr^{+++} and Nd^{+++}) the levels lying near the basic level might also take part in the transitions giving rise to phosphorescence spectra. Such levels have been found in every compound of these salts which we have investigated and should almost certainly be present in the phosphors. Absorption lines arising from them would show a strong change of intensity with temperature and thus would be partially masked due to the vibrational bands of the "activated centers" which also show such a dependence.⁹

F. H. SPEDDING

Chemical Laboratory,
University of California,
Berkeley, California,
December 13, 1932.

⁶ Spedding and Bear, *Phys. Rev.* **42**, 75 (1932).

⁷ Tomaschek, *Phys. Zeits.* **22**, 878 (1932).

⁸ Spedding, *Phys. Rev.* **38**, 2080 (1931); *ibid.* **37**, 777 (1931); Spedding and Nutting, *Phys. Rev.* **38**, 2294 (1931); *J. Am. Chem. Soc.* to be published February, 1933; Spedding, *J. Chem. Phys.*, to be published February, 1933.

⁹ It might be mentioned here that in the pure absorption spectra of the rare earth salts no vibrational bands of any sort are observed. We find only lines arising from electron transitions between levels which have been decomposed by the electric fields of the crystal.

The Efficiency of Electron Release by Metastable Atoms

In the period since the publication of the author's previous letter of this title¹ (referred to as I), a correction and a defense have become necessary.

The experimental facts are briefly these: The sparking potential in pure neon is decreased to perhaps a third of its value by the addition of traces of an impurity which may be ionized by excited neon atoms. Illumination of the spark in such impure gas with the light from a neon lamp increases the sparking potential to perhaps two-thirds the value for pure gas, but illumination does not affect the sparking potential in pure gas. The addition of N_2 to A or A-Hg mixtures produces effects exactly parallel to those of neon radiation on neon discharges.

In deducing the results of I, it was assumed tacitly that the spontaneous disappearance of metastables in the body of the gas was due to their return to the normal state in collisions of the second kind with normal gas atoms, the energy being converted into kinetic energy. (The evidence then available indicated that the difference in the rates of

diffusion of resonance radiation and metastables was too small to account for the observed magnitude of the effect of illuminating the discharge with light from a neon positive column.) Recently, Dr. Kenty of the G. E. Vapor Lamp Co. suggested in a private communication that the spontaneous disappearance of metastable atoms was due to their transfer to the resonance state by collisions of the first kind with normal atoms, the resonance radiation diffusing out of the region more rapidly than was previously believed.² On this view, the illumination of the region of the discharge merely accelerates the process of converting metastables into resonance radiation. Since the substitution of photons for metastables at the cathode has no effect on the discharge, the conclusion to be drawn is that the two have equal electron-emitting efficiencies. From the quantitative considerations of I, the difference in their efficiencies

¹ E. W. Pike, *Phys. Rev.* **40**, 314 (1932).

² C. Kenty, *Phys. Rev.*, February 1 (1933).