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The X-ray spectra and the structure of the atoms

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We all know that the discovery of X-rays provided the medical sciences with a new and invaluable working tool; and we must all be equally aware that recent developments in the study of X-rays have opened up new paths of investigation in various fields of the natural sciences. One can already point to a whole range of major problems which the use of X-rays has made it possible to solve.

It is obvious that the fact that X-rays are such an important tool for workers in various fields of science forms a very cogent reason for undertaking a thorough investigation of their nature.

It is also clear that, seen from this viewpoint, any investigation of X-radiation must be planned on a broad basis, and cannot be directed solely towards the more or less specialized problems affecting different branches of science.

The study of X-rays is not, however, motivated only by their application in the various sciences such as we have just mentioned. X-rays provide us in addition with an insight into the phenomena within the bounds of the atom. All the information on what goes on in this field of physical phenomena is, so to speak, transmitted in the language of the X-rays; it is a language which we must master if we are to be able to understand and interpret this information properly.

The phrases of the language, in this instance, are made up of electromagnetic waves, and the features of these which we are able to recognize, record, and interpret are in the first place the *wavelength* and *intensity* of this radiation. Experience has taught us that if we concentrate our attention on a particular atom, then a system of waves is emitted from this atom having an entirely fixed composition with respect to the wavelengths involved. These wavelengths are also, in practice, entirely independent of such external circumstances as the chemical or physical forces acting upon the atom concerned. The system of waves is governed solely by the field of force of the atom being studied.

The first task which faces us, if we seek to unlock the mystery of the

atom in this way, will therefore be to find some way of measuring and ana-
lysing the wave systems emitted by the atoms of the 92 different elements.

I should like, here, to comment on one point. The problem I have just
mentioned might well have been insoluble because of utter complexity in
the wave system. We have only to remember how, in the field of ordinary
optics, certain spectra are composed of tens of thousands of different wave-
lengths, and continue to defy all attempts at a preliminary classification.
Where the X-radiation from the atom is concerned, however, Nature has
been rather more accommodating. Not only are the wave systems peculiar
to each type of atom moderately complicated, but also the wave systems
belonging to the different atoms show considerable general agreement. This
agreement is not, as in normal spectroscopy, confined to the vertical groups
of Mendeleev's table, but extends to all elements.

It is noteworthy, therefore, that the general type in which X-ray spectra
occur has a far-reaching analogy with precisely the type in the normal spec-
tral range which is to be found in the first vertical group in Mendeleev's
table, i.e. the alkali spectra.

In order to be able to demonstrate this, I shall have to say a few words on
the subject of obtaining an energy diagram from the observed wave system.

Let us assume that at a given moment a certain atom is in such state that
its total energy has the value E_1. At that moment a rearrangement occurs
within the atom which has the effect of reducing the total energy to E_0. In
the course of this process of rearrangement the quantity of energy liberated
is therefore:

$$E_1 - E_0$$

We may assume, with Bohr, that this quantity of energy appears in the form
of a wave, making up part of the wave system which is characteristic for the
atom in question. Its wavelength we may term λ, with a corresponding fre-
quency ν, and we may define ν as the reciprocal value of λ, thus:

$$\nu = \frac{1}{\lambda}$$

According to the Einstein-Bohr formula there is thus a relationship between
the frequency ν_1 for the wave and the energy liberated from the atom:

$$v_1 = \frac{E_1 - E_o}{h}$$

where h is a universal constant (Planck's constant).

We can therefore imagine that the energy of the atom during a rearrangement of this nature, is then changed from E_2 to E_o, during which a wave of frequency v_2 is emitted. Thereby is

$$v_2 = \frac{E_2 - E_o}{h}$$

The series can be continued further:

$$v_3 = \frac{E_3 - E_o}{h}, \text{ and so on.}$$

By measuring the wavelengths it is possible experimentally to determine a series of v-values: $v_1, v_2, v_3, \ldots$ It would, however, require a special and not always simple analysis of the wavelengths available in order to select and bring together those frequency values which belong to one and the same series. The first person to succeed, within the field of normal spectroscopy,
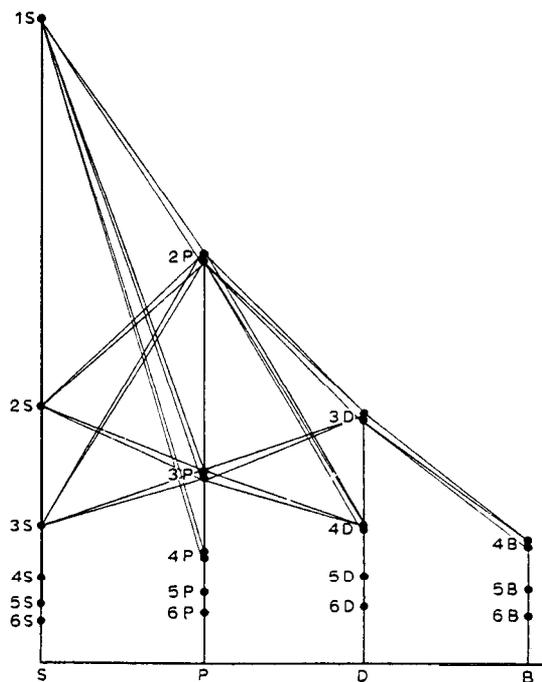

Fig. 1.

in solving this difficult, but for future research fundamental, problem was
the Swedish scientist J. R. Rydberg.

Rydberg, namely, found a general formula for the relationship between
v-values forming part of the same series, and he made use of this formula to
collect the different series for each separate element from the range of wave-
lengths available.

For the alkali spectra, in particular, Rydberg found three different series,
which he termed the principal series, the sharp, and the diffuse secondary
series. These three series have since been supplemented, through new meas-
urements, by a further series commonly known as the Bergman series.

If we now apply the Einstein-Bohr formula we can, by using the known
v-values, disentangle four series of energy values determined with high
exactitude relative to each other. These four energy-level series are usually
graphically represented as shown in Fig. 1. For each point, the height above
the horizontal base line is a measure of the amount of energy characteristic
of the state in question. These four series, each shown on a vertical line, are
usually termed the s-, p-, d--, and b-series. From the energy series we come
according to the formula

$$\nu_{\mathrm{I}} = \frac{E_1 - E_0}{h}$$

back to the frequency series (shown in Fig. 1 by the inclined lines).

What is characteristic for the optical spectra belonging to the first vertical
group of Mendeleev's table, i.e. for the alkali spectra, is the fact that of the
four energy series, the s-series consists of simple energy levels, while the
three remaining series, that is to say the p-, d-, and b-series, are made up of
double levels, as will be seen from Fig. 1 which represents the energy and
frequency diagram for potassium.

If we now switch from the optical spectra to X-ray spectra, an examina-
tion of the combined results of measurements indicates that the X-ray spectra
for all elements can be represented by an energy diagram of exactly the same
kind as was previously found for the alkali spectra. This diagram is shown in
Fig. 2. Apart from the energy levels corresponding to the s-, p-, d-, and b-
series (the vertical lines), there are the observed transitions, spectral lines rep-
resented by lines linking the two energy levels which correspond to the
initial and final state of the atom when the spectral line in question is emitted.
It follows from this that the main series in normal optics matches the K-series
in the X-ray spectra. The L-series, on the other hand, is put together from the

two secondary series in optics and a few other lines of the principal-series type.

The main reason for giving the energy diagram for X-ray spectra in this form is, that by doing so the rules of combination remain identical with those which apply to alkali spectra. In both cases, for instance, transitions occur only between two adjacent vertical series. There are, moreover, no transitions occurring within one and the same vertical series.

There were, additionally, a few very approximative estimates of the intensity of some of the X-ray lines, which seemed to suggest that the analogy not only applied to the rules of combination, but that in the case of intensity conditions as well there existed a certain agreement. If such is the case, then this provides particularly strong support for the diagram we have assumed.
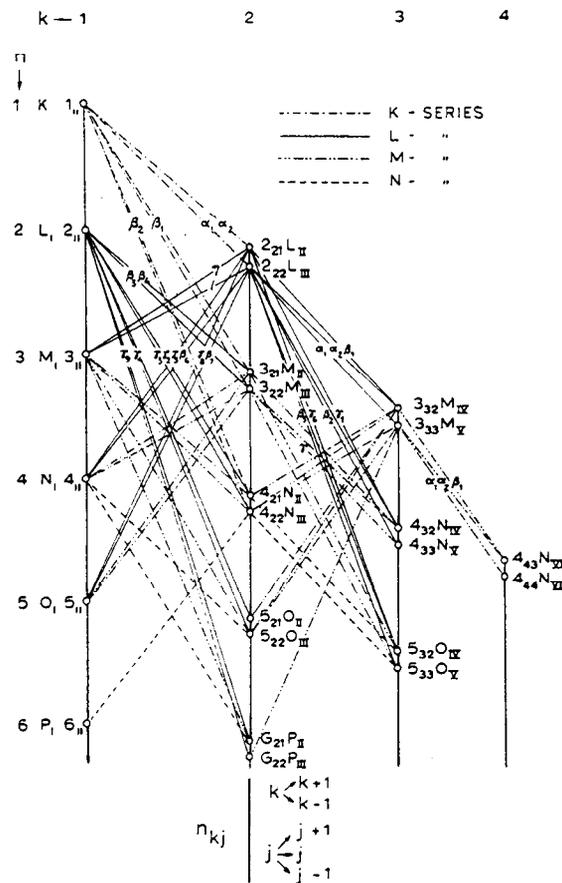

Fig. 2.

In passing judgment on this latter question we can now take into account the results of a study recently carried out by lecturer Axe1 Jonsson at the Uppsala Institute of Physics. Measurements made hitherto have referred to the X-ray spectra of tungsten and platinum, and they show, with one or two very minor exceptions, a very fine agreement with the intensity conditions in the optical alkali spectra. In some respects, otherwise, this result goes further and deeper than what is the case in the optical field, and the measurements can also be used to get a better insight in the mechanism of radiation itself than has been possible up till now.

If we bring together on the one hand the measurements of wavelength and on the other those ofintensity, then we have in them both strong support for the justification of the diagram shown.

What then is the further, deeper reason for the X-ray spectra exhibiting such a far-reaching analogy with the alkali spectra in particular? In fact, the answer is not so difficult to give. An alkali atom consists of an internally completed electron structure of the same type as that of the inert atom next to it, but has in addition a loosely bound valency electron. The optical spectrum is emitted when this loosely bound valency electron moves from one quantum orbit to another. For the X-ray spectra, too, we must assume that light emission takes place when an electron, but in this instance one belonging to the inner electron system of the atom, moves from one quantum orbit to another while the state of all the remaining electrons is not altered to any significant extent.

Quite irrespective of whether the energy diagram should be given this or some other form, X-ray spectroscopy measurements provide us with a quantitative and thorough knowledge of the energy content and energy relationships within each particular atom. Any further work on the structure of the atom must rest upon this firm, empirical foundation.

An energy diagram as complete as that shown in Fig. 2 is, however, only found for the heaviest elements. If we go further down the Mendeleev table towards the lighter elements, one level after the other will stepwise disappear until, when we reach helium and hydrogen, there is only a single energy level. This successive disappearance of the levels is seen in Fig. 3, which shows the diagrams for the inert gases. At the same time the figure shows how the number of X-ray spectrum lines successively decreases, so that for argon, for example, we only find four L-lines apart from the K-series, while there are only two K-lines for neon.

This way of representing the energy diagram for various elements also

gives us a good guidance when we have to extrapolate data from the field of X-ray spectroscopy to that of normal optical spectroscopy. It is then clear that only those spectrum systems in the optical field which allow a representation in the form of an alkali diagram can be considered as a continuation of X-ray spectra. The interpretations of line systems in the optical field as a continuation of known X-ray series which are proposed in some cases is contrary to this first, logical requirement.

Otherwise, the comparison of the diagrams indicates that the chances of rediscovering the actual X-ray series in the optical field are greatest for the heaviest elements, where a large number of levels with small differences in energy occur.
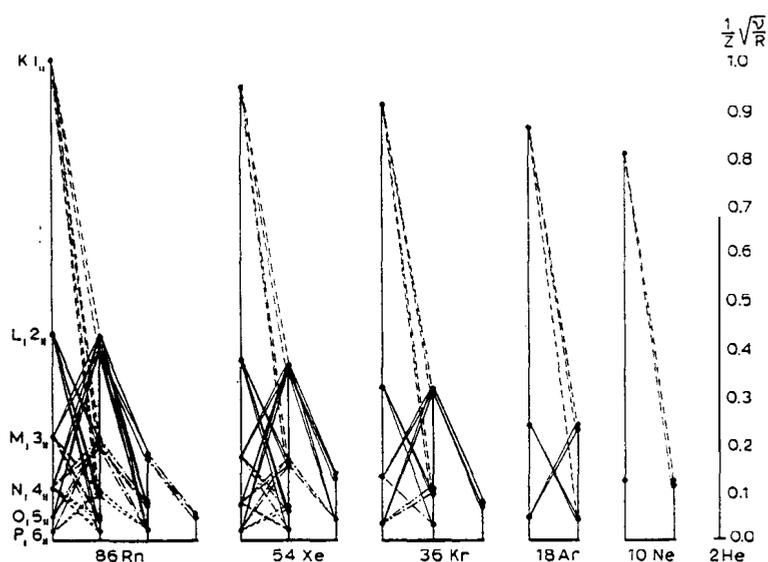

Fig. 3.

We may now ask ourselves whether this diagram of levels is merely a convenient and clear way ofrepresenting the results of observations, or whether the diagram, in this or some similar form, has a deeper significance. Thanks to the fact that we can in many cases determine with considerable accuracy the absolute energy value for a number of levels in the diagram, we are, by means of measurements of wavelength in the line spectrum, in a position to state the absolute energy values for all the levels. This diagram, which has now been given for the majority of the elements, thus supplies fundamental information on the energy state of the atom of each element. These are

primary natural constants which are obtained in this manner with the help
of X-ray spectroscopy. If we cast our minds back to the work that has, over
the years, been devoted to other atomic constants, such as the determination
of the atomic weight of the elements, and if we further consider that the
atomic weight of most elements is no more than an average value from dis-
continuously varying group values, and that this is not true of the energy
diagram of the elements, then I dare to feel that the efforts which have been
directed to finding this energy diagram for the atoms has been fully justified.

This has also, I should like to say, closed the first chapter in the history of
X-ray spectroscopy. This work has, however, given rise to new problems
which have now to be tackled. Recently, in a lecture to the Swedish Society
of Chemists, I drew attention to preliminary studies which are being made
in one of these new fields - the matter of the chemical properties of the
atoms having an effect upon the phenomenon of X-radiation.

I would like to close this lecture with a short report on a few recent results
in another field of study which stems from the X-ray spectroscopy meas-
urement we have been discussing. The very first accurate measurements of
X-ray wavelengths using the new precision methods showed us that the
accepted law of Bragg was not entirely exact. These experiments, originally
carried out by Dr. W. Stenström, were interpreted by him as indicating
that X-rays were diffracted when they passed through the surface of the
crystal being used as a grating. With the further increases in the accuracy of
measurement which have been attained since then, it has become possible
employing this method to make extremely accurate quantitative measure-
ments of the refraction of the X-rays in various crystals. The method has
also been used in a modified form by a number of American workers. In a
letter to the British journal *Nature* about a year ago, E. Hjalmar and I re-
ported on a number of results which seemed to indicate that the refraction
in a crystal underwent a discontinuous change when the frequency of the
radiation passed the characteristic frequency of the type of atoms making up
the crystal. That is to say, we suggested that the experiment must be con-
sidered as depending upon an anomalous dispersion.

The analogous phenomenon which has long been known in ordinary op-
tics, where it has been the subject of careful study, has proved to be of fun-
damental importance for an understanding of the mechanism of radiation
itself. It therefore seems to me to be of particular interest to try to find, in the
field of X-radiation, some more direct method of obtaining this effect, and
perhaps of making quantitative measurements. To this end civil engineer A.

Larsson at the Uppsala Institute of Physics has been making a number of experimental studies using the following method which will give a direct indication of any anomalous dispersion.

A suitably chosen line spectrum is recorded photographically, once with a copper-sulphate crystal and again with a calcium-sulphate crystal. If the spectrum selected is such that it contains spectrum lines on either side of the characteristic radiation frequency of the copper, any anomalous dispersion would betray itself as an irregular shift of the spectrum lines on the plate made with the copper-sulphate crystal compared to the position of the lines on exposure with the other crystal. The results of the exact measurements on the two plates have shown that such is the case. I should add, in conclusion, that the experiment was so arranged as completely to eliminate the differing absorption of radiation on either side of the characteristic frequency of copper.

The demonstration of anomalous dispersion in X-radiation has opened up a new path for further work, a path which seems likely to lead us to new data on one of the most urgent problems of atomic physics today - that of the distribution of electrons within the atom. Only continued experimental work can show how close this path will bring us to our goal.