ADDITIONAL LINES IN THE K SERIES OF MOLYBDENUM AND THE NATURAL BREADTH OF SPECTRAL LINES

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We have recently greatly improved the resolving power of the double X-ray spectrometer by turning crystal B so as to increase the angular reflection.¹ The first crystal A when set for a spectral line gives a parallel beam of strictly homogeneous rays. It acts as a collimator precisely as the collimating lens in the case of the light spectrometer. The second crystal B is then an analyser.

The degree of analysis depends on the perfection of the crystals. By means of this arrangement of the double X-ray spectrometer with the



two crystals set for first order reflection, we were able to obtain a considerable separation of the Mo K β doublet. At the same time Ehrenberg and Mark² and Ehrenberg and Susich³ had employed a similar arrangement of the double X-ray spectrometer for the purpose of measuring the natural breadth of spectral lines.

In the course of their experiments Ehrenberg and Susich also obtained a partial separation of the Mo K β doublet. The separation obtained, however, was not so complete as that obtained by ourselves. Our better resolution is perhaps due to the fact that we limited the vertical height of the slits. In the case of the double spectrometer with crystals arranged as in (a), figure

1, the sharpness of rocking curve is independent of the horizontal width of slits. The sharpness, however, is greatly affected by the vertical height of the slits. With the two crystals arranged in parallel as (b), figure 1, the sharpness of rocking curve is independent of both the vertical height and the horizontal width of slits. These facts are evident from the geometry of the arrangement and need not be discussed in detail.

In the previously described experiments the collimator and analyser were both set for first order reflection. We have continued these experiments using the crystals at second order reflection and in one case $(K\alpha_1)$ we have used them at third order. The resolving power increases with the order of reflection. This increase is due to two properties: (a) The increased angular separation for a given wave-length interval $d\lambda$. Since $n\lambda = 2d \sin \theta_n$, $nd\lambda = 2d \cos \theta_n d\theta_n$ for one crystal. For two crystals

$$2nd\lambda = 2d \cos \theta_n d\theta_n. \tag{1}$$

(b) The rocking curves become narrower at higher order reflection. This is made evident by comparing the widths at half-maximum of $K\alpha_1$ curve for first order given in our original paper (Fig. 2), with the second order curve, figure 3 in this paper. The widths are 31" and 22" of arc, respectively.

The crystals used are split calcite. The reflecting surfaces are the planes that were contiguous before splitting. The surfaces are carefully pre-



FIGURE 2

served from abrasion. Even touching the surfaces with the finger would probably increase the width of rocking curve.

We have investigated the K series of molybdenum at higher orders of reflection. Additional spectral lines have been observed near the β_2 line, and near the α_1 and α_2 lines. Owing to the small energy, the γ line could not be separated into its components, γ_1 and γ_2 , which should be present. The results obtained are shown in figures 2, 3, 4 and 5. The β_1 line has an extra line on the long wave-length side which is designated β'_1 . Its angular distance is 24" of arc from β_1 . The corresponding wave-length interval $d\lambda$ as calculated by (1) is 0.17 X-Unit. The second order curve for α_1 line is shown in figure 3. The extra component is 12" on the long wave-length side. The corresponding $d\lambda$ is 0.085 X-Unit. The results for α_2 are given in figure 4. The curve shows two components of the same height but differing in width, a sharp curve and one that is broader. The sharp curve we have provisionally assumed to represent the α_2 line. The more diffuse we have designated α'_2 . Its greater width indicates that it may not be a single line but may itself be complex. It would probably separate into components at higher order reflection.

It was attempted to investigate the α_1 line at third order reflection on both crystals. The curve obtained is given in figure 5. It shows the extra line α'_1 at 20" of arc from α_1 , equivalent to $d\lambda = 0.088$ X-Unit. This is in agreement with 0.085 X-U obtained at second order. The third order results are not so reliable. The curve is not a good one. Only a few points were obtained. The energy was too small to attain much accuracy.



These additional lines are probably not "fine structure" lines as the frequency interval $d\lambda$ is not constant. They are more probably "spark" lines arising from multiple ionization of the atom. This view is supported by the fact that the width of rocking curve at *first order* increased with the voltage. The curve for α_1 was quite narrow at a voltage of 22 kv. and progressively increased to about 35 kv. at which it was constant. The rocking curve at first order includes both lines. This increase of width with voltage indicates that the component α'_1 is very weak or absent at low voltages but comes in strongly with increased voltage, but that above 35 kv. the two components increase in the same ratio. This same effect of voltage on width of spectral line has been observed by Siegbahn and Larsson⁴ in the case of some lines in the L series of molybdenum. They attributed the change in width to the production of new components as the voltage increased.

Additional or "spark" lines have also been obtained for copper and nickel, using the collimator at second order and the analyser at first order reflection. Experiments are now in progress with both crystals at second order. The results will be published later.

Natural Width of Spectral Lines.—The observed width of a spectral line will depend on two conditions: (a) the actual width (frequency deviation present in the radiation), and (b) width arising from all instrumental defects and limitations.

The real width, for instance, might be expected to depend on the damping of electron oscillations due to radiation and on Doppler effect arising from



FIGURE 4

temperature agitation of the molecules. The Doppler effect can be shown to be negligibly small at the temperature of the target. If the radiating electron is an oscillator emitting stored energy, its amplitude of oscillation should progressively decrease with the time.

The energy⁵ lost in a time dt by a charge e having acceleration a is

$$E = \frac{2}{3} \frac{e^2}{c^3} \int a^2 dt.$$
 (2)

By means of this expression it may readily be shown that the value of the damping constant k defined by:

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$$A = A_{0}e^{-m}$$

$$k = \frac{4\pi^{2}e^{2}}{3c^{3}}\frac{\gamma^{2}}{m}.$$
(3)

is.

The complex wave form emitted by an electron so damped gives by means of the Fourier analysis a spectral line of finite width. The width^{6.7} of such a line at half-maximum is:

$$d\lambda = \frac{k\lambda^2}{\pi c},$$

or

$$d\lambda = \frac{4\pi}{3} \frac{e^2}{mc^2} = 0.00012 \text{ Å} = 0.12 \text{ X-Unit.}$$

The width is independent of the wave-length.



The experimental curves for the lines given in figures 3 and 5 have been resolved into the components α_1 and α'_1 . These components are represented by the broken lines in the figures. The principal component (α_1) at second order is 15" wide at half-maximum. This width expressed in terms of $d\lambda$ by equation (1) is 0.103 X-Unit. This same component is 20" wide in the case of third order reflection. This angular width expressed in terms of $d\lambda$ is 0.088 X-Unit. On account of the difficulty of obtaining the third order curve these results may be considered to be in agreement. They indicate that the width of the components do not appreciably decrease with increase of order. Except for the contributions of crystal imperfections, these components would represent the natural width of the spectral lines.

The two crystal methods of measuring the width of spectral lines has been used by Ehrenberg and Mark and Ehrenberg and Susich (l. c.). In principle a rocking curve obtained with crystals arranged as in (a), figure 1, shows the natural width plus the effect of crystal imperfection plus the effect of vertical height of slit, when the crystals are placed parallel as (b), figure 1, the rocking curve is independent of line width and of vertical height of slit. The curves in this position are only affected by crystal imperfection. In addition the curves in both positions would have a width arising from the Fresnel interference bands which depend on the number of grating elements taking part in the reflection.

Ehrenberg and Mark (l. c.) have corrected for the error in width of curve obtained at position (a) by taking a correction curve at position (b). They derive the following expression for this correction:

$$H_{\lambda} = \sqrt{H_2^2 - H_1^2} \frac{2d}{2n} \cos \theta_n \tag{4}$$

where H_2 is angular width of curve at half-maximum obtained at position (a) and H_1 is the width obtained at position (b).

Their experiments were made with both crystals at first order. The width H_{λ} obtained was greater than is to be expected from the damping of an electron by its own radiation. The greater width observed by these experimenters may be due in part to the presence of the "spark" lines. They were not measuring a single emission line, but at least two lines near together. It is not certain in our experiments that we have obtained single emission lines. Higher resolving power might show still other components.

The angular width of the main component of α_1 at second order is 15" of arc. This is the value of H_2 to be introduced into equation (4). A measurement was then made of H_1 at parallel position (b). This curve was so narrow that even to find it was a matter of great difficulty involving a search of several days. Its measured width was 3.75" of arc. The width H_{λ} obtained is 0.1 X-Unit for the principal component of α_1 measured with both crystals at second order. At third order reflection the principal component α_1 is 20" wide (Fig. 5). The correction term H_1 was not measured. It is certainly less than 3.75" of arc. Using the value of H_1 obtained at second order the value for H_{λ} at third order is 0.088 X-Unit. It is difficult to state definitely that this is a real decrease with order. The precision of measurement at third order was much less than at second order. In addition the graphical representation of a curve by two component curves is not precise. The smaller component representing α'_1 at both second and third order is narrower than the component α_1 . If the α_1 and α'_1 components are each single lines they should be of the same width. We are not able to draw two symmetrical components of the same width that would sum to the observed curve. It is possible that the principal component is not a single line but may be itself complex.

These results suggest that the natural width of a spectral line may be less than the value to be expected from the classical theory of damping by radiation.

The subject of width of spectral line is one of considerable importance. If the lines are really much narrower than 0.12 X-Unit the radiation cannot come from a damped oscillating electron. The mechanism must be such as to maintain a pure harmonic oscillation of constant amplitude until the quantum of energy is completely emitted. Such a train of waves would need to have a great number of elements and so have considerable length. An alternate hypothesis would be that a quantum is an entity (the word "pulse" is avoided) that may be resolved into a train of waves by the crystal grating. In this case the width of a spectral line would depend on the degree of perfection of the crystal. The quantum theory of crystal grating action advanced by Duane⁸ might also give a narrow spectral line, whose width would be a property of the crystal grating and not of the radiation.

¹ Bergen Davis and Harris Purks, Proc. Nat. Acad. Sci., 13, No. 6, June, 1927.

² Ehrenberg and Mark, Zeits. Phys., 42, May, 1927.

* Ehrenberg and Susich, Ibid., 42, May, 1927.

⁴ Siegbahn and Larsson, Ark. Math., Ast, Eysik., 18, No. 18, 1924.

⁴ Larmor, Ether and Matter, page 229.

⁶ G. E. M. Jauncey, Phys. Rev., 19, Jan., 1922.

⁷ A. H. Compton, X-Rays and Electrons, p. 56.

* W. Duane, Proc. Nat. Acad. Sci., 9, 158 (1923).

THE CORRESPONDENCE PRINCIPLE IN THE STATISTICAL INTERPRETATION OF QUANTUM MECHANICS

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In studying the very significant statistical interpretation put on the quantum mechanics by the "transformation theory" of Dirac¹ and Jordan,² the writer at first experienced considerable difficulty in understanding how the quantum formulas for averages and probabilities merge into the analogous classical expressions in the region of large quantum numbers and also, of course, in the limit h = 0. In the present note we shall aim to trace through the asymptotic connection between the formulas of the two theories, which does not seem to have been quite adequately elucidated in existing papers.

In the transformation theory a diagonal element of a matrix which