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The Identification of Characteristic X-Rays Associated with Radioactive Decay

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An investigation has been made of the practicability of employing a bent rocksalt crystal spectrograph in the identification of x-rays emitted during radioactive decay. The spectrograph has been found to be a useable tool. X-rays associated with the disintegration of ${}_{31}\mathrm{Ga}^{67}$ ${}_{29}\mathrm{Cu}^{64}$, ${}_{35}\mathrm{Br}^{80}$ and ${}_{43}\mathrm{Ma}$ have been identified.

INTRODUCTION

RECENTLY it has been discovered that as a result of electron capture by the nucleus or internal conversion, many radioactive atoms emit characteristic x-rays in the process of disintegration. Alvarez,[1,2] who first demonstrated electron capture, has pointed out that many such cases should be found. He has also found internal conversion in Ga^{67}, where the coefficient is surprisingly high. Dancoff and Morrison,[3] in examining the theory of internal conversion for lighter elements, find that for energies less than 0.5 Mev and highly forbidden transitions, the coefficients may be $\gg 1$.

These writers point out eight instances of internal conversion. Additional examples have since been found, and it is quite probable that a systematic search would reveal a large number of such cases. A knowledge of the properties of x-rays emitted by decaying atoms can throw illumination upon the processes which are occurring. Thus, if a substance chemically identified as atomic number Z gives off characteristic radiation of an element $Z-1$ and no positrons, the process occurring is electron capture which may or may not be followed by internal conversion. If characteristic x-rays of element Z are emitted, one is dealing with nuclear isomerism. If the radiation is to be identified with an element $Z+1$, the process occurring is emission of a continuous beta-spectrum followed by internal conversion as the nucleus of element $Z+1$ falls from an excited to a lower state. In many cases the best method available for deciding between the three possibilities is identification of the x-rays which are given out in the process.

EXPERIMENTAL METHODS

Two methods are generally employed for identification of these x-rays—measurement by absorption, or by diffraction from a crystal. By far the best absorption method, and one which is usually adequate for needs of nuclear physicists, is that involving the use of critical absorption. When called upon to identify the radiation associated with any given radioactivity, the investigator knows that he is dealing with the characteristic x-rays of one of several elements. His measurements merely decide among the several possibilities.

The method of critical absorption has a number of disadvantages: Thin foils of most elements are not available; some of the elements needed are costly and difficult to obtain; the method works well only when the x-rays present belong to one element, and measurements carried out on complex radiations give confusing results. Clearly, then, the merits of the diffraction method for identification of x-rays bear investigation. In considering the practicability of using a diffraction method for identification of x-rays, the main question is one of intensities. Even with the tremendous intensities of radioactive materials available from the cyclotron, use of an ordinary x-ray spectrometer is impractical. The present work, however, has shown that by employing a bent crystal spectrograph, present intensities are sufficient to obtain pictures of x-ray lines from many elements.

BENT CRYSTAL SPECTROGRAPH

Some of the principles of design of a bent crystal spectrograph were discussed by DuMond

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[1] L. W. Alvarez, Phys. Rev. 52, 134 (1937).

[2] L. W. Alvarez, Phys. Rev. 54, 486 (1938).

[3] S. M. Dancoff and P. Morrison, Phys. Rev. 55, 122 (1939).

and Kirkpatrick[4] in 1930. Johann[5] described a bent mica crystal spectrograph which he used successfully. Mlle. Cauchois[6] employed spectrographs having bent mica and gypsum crystals. Johansson[7] constructed a bent crystal spectrograph in which the crystal was both bent and cut in order to secure perfect focusing. Others have employed the bent crystal spectrograph for investigations of weak x-ray lines. The bent rocksalt crystal spectrograph used in the present investigation is essentially that described by Bozorth and Haworth.[8] The arrangement employed is shown in Fig. 1. Corresponding to any given wave-length λ there is a certain angle θ for reflection given by the well-known Bragg law:

$$n\lambda = 2d \sin \theta.$$

Here, since first-order reflection is used, n is one. If a radioactive sample which emits x-rays is placed along the focal circle, those rays satisfying the Bragg condition and striking the crystal will be brought to a focus on the focal circle on the opposite end of the crystal. Theoretically, in using x-ray film for a detector, one should bend the film to conform to the focal circle. However, by placing the film perpendicular to the x-ray beam, the radiant energy is concentrated on a smaller area. The energy per unit area (on which the x-rays fall) is increased by a factor of approximately $1/\sin \theta$. Part of this increase is offset by the fact that the x-rays pass through a smaller thickness of film and are hence less completely converted. Moreover, the film is supposedly in focus for only one λ. However, if one is seeking to identify radiation as being that of one of three neighboring elements, a lack of focal depth is not a serious handicap because the line width due to imperfections of the crystal is large enough to minimize the importance of the added width introduced through improper focusing.

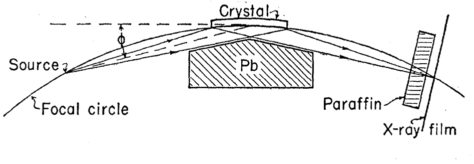

FIG. 1. The bent rocksalt crystal spectrograph. The crystal is bent to a radius of 30 cm and cut to a radius of 15 cm.

In this work two spectrographs were used. To obtain the lines from Ga^{67} and Cu^{64}, a spectrograph whose radius of focal circle was 15 cm was employed. This spectrograph was equipped with a crystal 2 cm by 3.2 cm, and the intensity of reflected radiation was quite high. Investigation showed that no ghost lines were obtained. The major imperfection lay in the width of the line appearing on the plate. This was associated with the fact that the image position was to a slight extent a function of source position. Through use of a fluorescent source of zinc x-rays, it was found that movement of the source could result in a displacement of the image by a distance corresponding to 0.02A. Since the separation of Zn and Cu is 0.11A, such a displacement is not serious. However, to eliminate possible artifacts through displacement of image, owing to displacement of source, special precaution was taken. When exposing the film to x-rays from a radioactive source, the source was made to cover a region on the focal circle corresponding to the three possible wave-lengths. In calibrating the film, the precaution was taken of having the fluorescent source cover the same region of the focal circle as was covered by the radioactive material. Under these circumstances any displacement of image with source is corrected for, since the calibration line and the line due to the radioactive substance are displaced in exactly the same amount.

The second spectrograph employed has a focal circle radius of 30 cm. The crystal, which is 3.4 cm long and 3.2 cm high, was supplied through the kindness of R. M. Bozorth. The characteristics of this spectrograph are quite different from those of the first one described. The principal disadvantages are lower intensity and the appearance of a ghost. The lower intensity arises from purely geometrical conditions, since in this case the source and image are farther removed by a factor of two. The ghost, which has an intensity about one-tenth that of the principal line, is well separated from it.

By taking the precaution of employing the same region of the focal circle as a source in

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[4] J. W. M. DuMond and H. A. Kirkpatrick, Rev. Sci. Inst. **1**, 88 (1930).

[5] H. H. Johann, Zeits. f. Physik **69**, 185 (1931).

[6] Y. Cauchois, J. de phys. et rad. **3**, 320 (1932).

[7] T. Johansson, Naturwiss. **20**, 758 (1932).

[8] R. M. Bozorth and F. E. Haworth, Phys. Rev. **53**, 538 (1938).

obtaining the line from the radioactive material and in calibrating, the danger of a fictitious result is eliminated. The advantage of this spectrograph is its good resolving power. Moreover, the image line is practically independent of source position. In a test it was found that tellurium and antimony K_α are readily resolved. This spectrograph should be useful in determining x-ray wave-lengths as short as 0.35A. Elements emitting such K_α x-rays (K_α of $P^{59}=0.348A$) also send forth L_α radiation with a wave-length less than 2.5A. It is quite practical to identify L_α radiation in an air spectrograph for elements above 59 in atomic number. Accordingly the range in which a bent crystal spectrograph is useful at present appears to be from atomic number 23 to 92. By use of a vacuum, this range could be extended somewhat.

EXPERIMENTAL RESULTS

Ga^{67}

The first x-rays examined with the spectrograph were those emitted in the decay of Ga^{67}. By critical absorption measurements, Alvarez[2] has shown that the radiation emitted by this activity can be described as characteristic zinc x-rays. This result was confirmed by the spectrograph,[8] and lines due to zinc K_α and zinc K_β were obtained. The calibration lines were obtained from copper and zinc. These elements were placed in the proper position on the source side of the focal circle and were exposed to continuous radiation from an x-ray tube. While the calibration lines were being obtained, the central portion of the film was shielded by lead. The 84-hour Ga^{67} was formed by deuteron activation of zinc. Gallium was extracted from the active zinc by means of a well-known ether extraction. The ether was evaporated to a volume of one cc, and the evaporation process was completed by allowing the ether to drop slowly upon a small piece of filter paper, thus transferring the gallium activity to the paper. The zinc bombarded was extremely pure, and it was not necessary to add gallium as a carrier. Accordingly the gallium activity present on the filter paper was free from elements which might have a large absorbing effect. The paper was of such length (1.5 cm) that when placed on the focal circle it covered the region corresponding to $\lambda=1.5A$ to $\lambda=1.2A$. When exposing the film to radiation from Ga^{67} the calibration portion was, of course, covered with lead. The length of exposure of the film to the x-rays from the active substance was generally of the order of twice the half-life of the material.

Br^{80}

Another problem which can be solved by diffraction methods is the question of x-rays emitted during the decay of the 4.5-hour Br^{80}. These x-rays were found by A. H. Snell (unpublished) during the summer of 1938. Absorption measurements showed that the radiations were absorbed strongly by arsenic and weakly by selenium. According to the values of the wave-lengths of x-rays given by Siegbahn, the radiation could be either bromine or krypton. From the facts known at that time there was no strong reason for identifying the radiation with one of the two elements. Accordingly, the radiation was examined by the spectrograph and shown to be characteristic of bromine.[9] This provided a strong clue that the 4.5-hour Br^{80} was undergoing an isomeric transition to some other state. Segrè, Halford and Seaborg[10] have shown by means of an isomer separation that the 4.5-hour body decays into an 18-minute substance. Hence the x-rays result from the internal conversion of a gamma-ray which is emitted in the transition of the Br^{80} from the energy state corresponding to the 4.5-hour to an energy state corresponding to the 18-minute body. The energy of the γ-ray has been measured[11, 12] and the presence of x-rays confirmed.[12, 13]

The active bromine was obtained through irradiation of brombenzene by neutrons produced by a 100-μa hour bombardment of beryllium by deuterons. Active bromine was extracted from the brombenzene with water. Sodium sulfite was added to the aqueous solution together with silver nitrate. The resulting silver bromide precipitate was very thin, weighing a few milligrams per cm^2. This is important because self-absorption can cut

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[9] P. Abelson, Phys. Rev. **55**, 424 (1939).

[10] E. Segrè, R. S. Halford and G. T. Seaborg, Phys. Rev. **55**, 321 (1939).

[11] G. E. Valley and R. L. McCreary, Phys. Rev. **55**, 666 (1939).

[12] R. E. Siday, Nature **142**, 681 (1939).

[13] L. I. Roussinow and A. A. Yusephovich, Phys. Rev. **55**, 979 (1939).

the intensity considerably. It is to be remembered that the average path the x-rays traverse in the source is $T/2 \sin \theta$ where T is the thickness. In exposing the film to the x-rays emitted by the bromine, it is necessary to eliminate the effect of scattered electrons. This could be done by use of a magnetic field or by selective absorption of the beta-particles. The latter method was employed; most of the electrons were absorbed in a 0.7 cm thick layer of paraffin, while the x-ray intensity dropped to a half. The silver bromide filter paper source was placed on the focal circle in such a way as to cover the region $\lambda = 1.15$A to $\lambda = 0.95$A, that is, the region corresponding to selenium, bromine and krypton K_α.

Cu^{64}

A third example of the use of the spectrograph was in the examination of the x-rays[9] emitted in the decay of Cu^{64}. Van Voorhis showed that a 12.8-hour activity is to be identified with Cu^{64} and that this body possesses a branching disintegration decaying either to Zn^{64} by negative electron emission or toe Ni^{64} by positron emission. Alvarez[2] later showed that x-rays were also associated with the decay of Cu^{64}. These x-rays were assumed to arise from electron capture, but no attempt was made to identify them. By use of the spectrograph the x-rays emitted by Cu^{64} have been shown to be characteristic nickel radiations. It appears, therefore, that Cu^{64} may decay by the three processes of negative electron emission, positron emission or electron capture. It could be argued that the nickel x-rays do not arise from electron capture but come as a result of internal conversion of a gamma-ray emitted after positron emission. However, the ratio of x-rays to positrons is close to that predicted on theoretical grounds.

In getting the picture of the x-rays from Cu^{64} the source was metallic copper itself which had been activated by 50μA hours of 8.0-Mev deuterons in the cyclotron. The source was placed on the focal circle covering a portion corresponding to $\lambda = 1.40$A to $\lambda = 1.70$A. In this case the best method of eliminating fogging due to beta-rays is certainly a magnetic field. However, even with the nickel radiation, it was possible to absorb almost all beta-rays with paraffin while cutting x-ray intensity to one-fourth. The spectrograph has since been rebuilt to facilitate use of a magnetic field for eliminating background due to beta-rays.

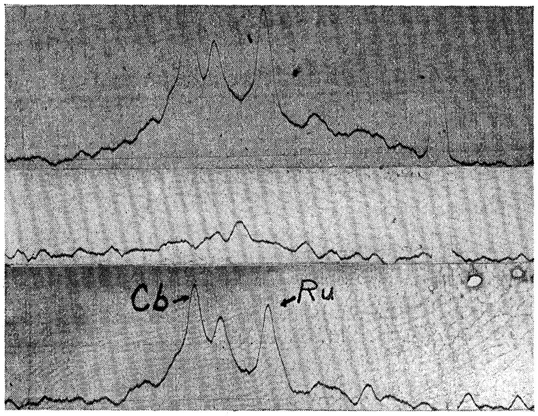

FIG. 2. A microphotometer trace of the K_α line of element 43. The three peaks of the upper and lower calibration traces correspond to the Cb, Mo and Ru K_α doublet. The main peak of the center trace is due to the K_α of element 43. The peak to the left is due to Mo K_α which arises from a two-day masurium activity.

The K_α line of element 43

A fourth picture obtained by the spectrograph was the K_α line of element 43. A microphotometer trace of this line is shown in Fig. 2. This radiation is associated with the decay of a 66-hour molybdenum activity which exhibits a branching decay. Of the order of one-fifth of the active molybdenum atoms disintegrate into a 6.6-hour masurium which drops to a lower energy state by gamma-ray emission. Another fraction of the molybdenum decays into a short-lived masurium which drops to a lower energy state by gamma-ray emission. In both cases the gamma-rays are internally converted and as a result characteristic x-rays of masurium are emitted. Segrè and Seaborg[14] have identified these radiations by critical absorption.

Because of the small intensity of x-rays (the internal conversion coefficient appears to be small) it was necessary to bombard the molybdenum 400μA hours with 8-Mev deuterons. The element was dissolved in nitric acid and precipitated with oxyquinoline following a procedure worked out by Perrier and Segrè.[15] The

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[14] E. Segrè and G. T. Seaborg, Phys. Rev. **54**, 772 (1938).

[15] C. Perrier and E. Segrè, J. Chem. Phys. **6**, 155 (1939).

oxyquinoline precipitate was converted into molybdic oxide and placed on the focal circle to cover a wave-length region from 0.74A to 0.62A. This chemical procedure is desirable because deuteron bombardment of molybdenum yields a number of masurium activities. Among these is a two-day body which strongly emits molybdenum radiation probably as a result of electron capture.

I wish to thank R. M. Bozorth and the Bell Telephone Laboratories for the gift of a rocksalt crystal and Dr. L. W. Alvarez and Dr. E. Segrè for their advice and suggestions. I wish especially to thank Professor E. O. Lawrence, under whose direction this work was carried out, and the Research Corporation for financial support.

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On the Single Crystal X-Ray Diffraction Pattern of Calcite

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The method of analysis of double spectrometer rocking curves developed by L. P. Smith is reconsidered. Although from Smith's very general viewpoint, six experimental curves are needed for a complete analysis, it is shown that for rocking curves from calcite, taken with the usual type of double spectrometer, it should be possible to deduce the shape of the single crystal diffraction pattern from two rocking curves, the $(1,+1)$ and $(2,+2)$. A method of modifying the equations of the instrument to allow for a simple type of mosaic structure is indicated.

The equations have been applied to rocking curves of Mo $K\alpha_1$ from calcite, supplied by L. G. Parratt. The method requires resolution of the observed curves into Fourier components, and a numerical method of doing this is described. The reliability of the components obtained can be tested by predicting the $(1,-1)$ curve with them and comparing with experiment. In this way it is found that the curves are consistent as regards Fourier components of long period and large amplitude, but inconsistent in the short period, small amplitude components. A single crystal pattern is deduced, based mainly on the observed $(1,-1)$ curve, with asymmetry as indicated by the $(1,+1)$ and $(2,+2)$ curves. It indicates that the crystals used do not have the flat-topped Darwin-Ewald-Prins diffraction pattern. Possible causes of the short period discrepancy have been investigated, but an adequate explanation has not been found.

Introduction

The object of this work is to determine, from observed two-crystal spectrometer rocking curves, the shape of the single crystal x-ray diffraction pattern applicable to a certain pair of calcite crystals. This function, $g(\theta)$, represents the fraction of the incident intensity of a beam of parallel, monochromatic x-rays which is reflected by the crystal when incident at a glancing angle differing by θ from the corrected Bragg angle. Knowledge of $g(\theta)$ is desirable for two reasons. First, a comparison may be made with the Darwin-Ewald-Prins[1] theory. Such a comparison should shed valuable light on the nature of the imperfection of an almost-perfect crystal. Second, $g(\theta)$ may be applied as a correction to measured wave-length distributions. Because $g(\theta)$ has a finite width, an observed emission line, absorption edge, etc., is always distorted by the crystals. Data such as those of Parratt[2] show that the distortion is not a simple process, and knowledge of the entire shape of the diffraction pattern is therefore needed to make the correction. Although for many purposes crystals may be found, such as etched quartz, which possess adequate[3] resolving power in the second or even the first order, occasions arise when, because of intensity difficulties, imperfect crystals must be used. An example is the use of the two-crystal spectrometer as an approximate

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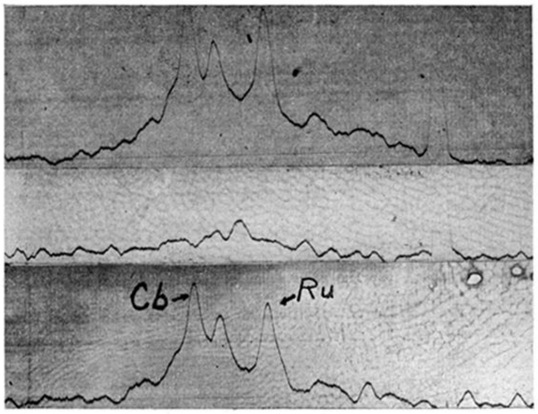
* Now at Rutgers University.

[1] C. G. Darwin, Phil. Mag. **27**, 325 and 675 (1914); P. P. Ewald, Ann. d. Physik **54**, 519 (1917), Zeits. f. Physik **2**, 232 (1920), Physik. Zeits. **26**, 29 (1925); J. A. Prins, Zeits. f. Physik **63**, 477 (1930).

[2] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

[3] L. G. Parratt, Phys. Rev. **46**, 749 (1934).



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