

# ANALYSIS OF SOME INDIAN ORES AND MINERALS BY BENT MICA CRYSTAL SPECTROGRAPH\*

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(Received for publication, April 26, 1955)

**ABSTRACT.** A transmission type bent mica crystal X-ray spectrograph has been constructed in which each wavelength chooses its own Bragg angle, and X-ray spectrum from Fe to U could be taken in one set-up. With the help of this instrument the presence of trace elements in some Indian ores and minerals has been studied, and some new results have been obtained.

## INTRODUCTION

To detect the presence of the unknown trace elements in ores and minerals with the help of a plane crystal Bragg spectrograph, a large number of X-ray spectral photographs are to be taken by setting the crystal at different sets of Bragg angles corresponding to  $K_{\alpha}$ ,  $L_{\alpha}$ , etc., lines of the different elements in question. The time of exposure should be of considerable length in each case. Replacing the traditional Bragg spectrograph by a bent mica crystal spectrograph designed by Mille Cauchois, we overcome these two difficulties, because in the latter case each wavelength chooses its own Bragg angle, and the time of exposure less than a minute is equivalent to one hour exposure with the usual Bragg method. Thus, on a single photograph we get a complete X-ray spectrum within a very short period of time from  $FeK_{\alpha}$  to  $SbK_{\alpha}$ . By chemical analysis and by optical spectroscopic methods, trace elements are usually detected; but chemical analysis is a lengthy and laborious process and optical spectroscopic methods are sometimes too laborious. Whereas, in the method described here, if once the line  $K_{\alpha_2\alpha_1}$  of a particular element is determined, then there is no ambiguity about the presence of the element in the ore. Compared to optical methods, identification of lines is very easy in this case.

## EXPERIMENTAL TECHNIQUE

The spectrograph was constructed following the outlines sketched by Mille Y. Cauchois, (Cauchois, 1932). The grating had a radius of curvature of 50 cms, and that of the film holder was 25 cms. The bent crystal holder and the cassette have been locally constructed and the final finishing of the cylindrical surface of the bent crystal holder was done by hand-lapping to eliminate the ghost lines. The whole system was placed on a circular disc resting on three adjustable screws. The circular disc was graduated in degrees. The grating holder was

\* Communicated by Prof. S. N. Bose.

rigidly fixed with it, while the film holder could be moved to different regions, to get the spectrum of that particular region.

On a copper target some known elements e.g., Ni, Zn etc. are rubbed to get  $K_{\alpha_2, \alpha_1, \beta_1}$  lines of the elements. The absorption edges of Br and Ag also appear

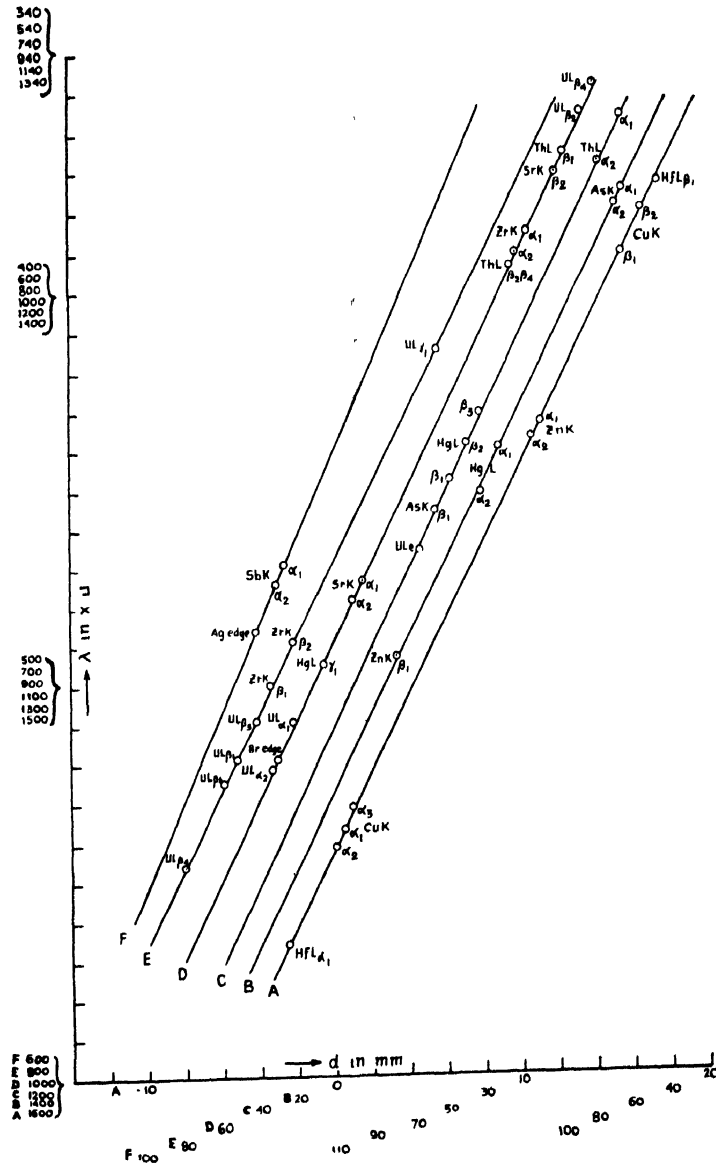


Fig. 1

Abscissa—distance measured in mm from  $CuK_{\alpha}$  line  
 Ordinate— $\lambda$  in XU.

on the X-ray film. Distances  $d$  in mms of different characteristic wavelengths are measured from  $CuK_{\alpha_2}$  to each of these lines or edges, and wavelengths for

each case being known from Seigbahn's data considering order correction, a graph is drawn, plotting  $d$  on one axis and  $\lambda$  on the other. The graph is very nearly a straight line (figure 1).

Now for each ore in question, the same process is repeated; and due to the presence of all the elements having atomic numbers greater than 26, characteristic lines are obtained. Measuring the distance of each line from  $\text{CuK}_{\alpha_2}$ , with the help of the  $d-\lambda$  graph originally drawn, the  $\lambda$  is determined. The dispersion obtained by the instrument used is approximately 10XU/mm on the photo-film.

The main beauty of this method of analysis lies in the fact that one should never fail to detect the presence of any element between 26 and 92 in the unknown ores and minerals, even if they be present in traces.

Pure  $\text{ZrO}_2$  was analysed and with an exposure of about 4 hours the minute trace of Hf was clearly detected. The period of exposure was too high because the operating voltage had to be kept low at 14 kv. for reasons explained below.

Sometimes it has been felt necessary to control the voltage of the X-ray tube so as to avoid the overlapping of emission lines of two different elements, as for example Hf  $L_{\alpha_1}$  (= 1566) and Zr  $K_{\alpha_1}$ , in second order (= 1568). So, to obtain Hf  $L_{\alpha_1}$ , the voltage applied was kept below the K-excitation potential of Zr.

#### SETTING OF THE SPECTROGRAPH

By different screw-adjustments the grating-holder could be given all sorts of movements and inclinations. In order to get photographs, the axis of the cylinder containing the grating-holder and that of the cylinder containing the film-holder must be parallel to each other. The different screw adjustments mentioned above serve this purpose. By using a spirit level and a plumb-line first of all the axes of these two cylinders were made parallel, each being perpendicular to the horizontal level. Then the diameters of the two cylinders were made coincident by optical methods. Mica was used for the crystal. A clean, optically flat mica piece was chosen for this purpose, and a particular plane in the mica which makes an angle  $\alpha = 10^\circ 19' \pm 1'$  with the split plane, was used as the Bragg reflecting plane. The orientation of this particular plane was determined by taking a Laue photograph of the mica piece. Then the mica was cut in proper size and was pressed inside the crystal holder, taking care that the curvature was perfect. For mica  $d = 2.554 \pm 0.005 \text{ \AA}$  and Cu  $K_{\alpha}$  lines were expected at an angle of about  $56^\circ$  from the direct beam. Although in one set-up a full X-ray spectrum is obtained in this case due to divergent beam used,—when trace elements are searched, it is desirable that the spectral lines due to the presence of these trace elements be of considerable intensity. As such, instead of taking the photograph in one set-up, sometimes two or three X-ray spectral photographs were necessary, the whole spectroscope including the grating-holder was differently oriented in each case, with respect to the direct beam.



Fig. 2  
Bent mica crystal X-ray spectrograph

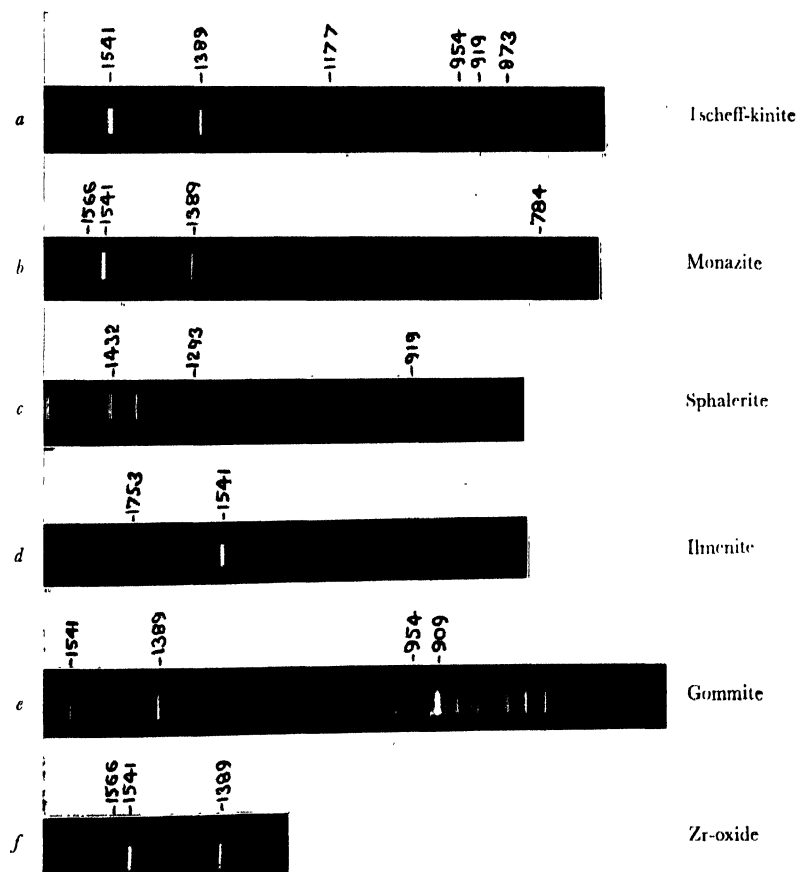


Fig. 3

RESULTS

The first X-ray photograph was obtained by using a clean Cu-target.. The original  $d-\lambda$  graph was drawn from the following lines :

CuK $\alpha_1$  ( $\lambda$ 1541 XU), CuK $\alpha_1$  (1537), CuK $\alpha_3$  (1531), ZnK $\alpha_2$  (1436), Zn K $\alpha_1$  (1432), CuK $\beta_1$  (1389), Cu K $\beta_2$  (1378), Zn K $\beta_1$  (1293), HgL $\alpha_2$  (1250), HgL $\alpha_1$  (1239), HgL $\beta_1$  (1047), HgL $\beta_2$  (1038), Hg L $\beta_3$  (1030), Br-edge (919), and Ag-edge (486).

The  $d-\lambda$  graph (figure 1) is split up into six graphs in order to magnify the scales. One small scale division is equal to one XU and the identification of different lines are correct to  $\pm 1$ XU.

With the help of  $d-\lambda$  graph thus obtained the unknown spectral lines of several ores and minerals were determined, as shown in Table I.

TABLE I

Serial No.	Name of ore	Tube voltage kv	Tube curr. ma	Time of exp. hours	Identified lines with $\lambda$
1	Tschoff-Kinite (Orissa)	32	5 -7	1	As K $\alpha_2\alpha_1\beta_1$ (1177, 1173, 1055) Th L $\alpha_2\alpha_1\beta_2\beta_1\beta_1$ (966, 954, 792, 764) Sr K $\alpha_2\alpha_1\beta_2$ (878, 873, 769)
2	Monazite (Travancore)	30	5	1	Hf L $\alpha_1\beta_1$ (1566, 1371) Zr K $\alpha_2\alpha_1\beta_1\beta_2$ (789, 784, 700, 689)
3	Sphalerite (Jawar mines, Udaypur)	32	5-7	1	Zn K $\alpha_2\alpha_1\beta_1\beta_2$ (1436, 1432, 1293, 1281) Sb K $\alpha_2\alpha_1$ (474, 469)
4	Ilmenite (Sumji, Singbhum)	32	5-7	1	Fe K $\beta_1$ (1753)
5	Gommite (?) (Rajputana)	32	6-8	2	U L $\alpha_2\alpha_1\beta_2\beta_3\beta_3\beta_1\beta_3\gamma_1$ (1065, 921, 909, 753, 746, 725, 719, 709, 614) Th L $\alpha_2\alpha_1$ (966, 954)
6	Zr -oxide (pure)	14	5	4	Hf L $\alpha_1$ (1566) Zr K $\alpha_2\alpha_1\beta_1\beta_2$ (789, 784, 700, 689)

A few interesting spectrograms are reproduced in figure 3 and the photograph of the spectrograph is reproduced in figure 2.

CONCLUSION

A thorough analysis of quite a large number of Indian ores and minerals have been undertaken and it is interesting to note that in many cases we are getting definite proof of the presence of certain elements in ores and minerals which have not been reported earlier by their chemical or spectroscopic analysis.

ACKNOWLEDGMENTS

The author is grateful to Prof. S. N. Bose for his kind help and encouragement. His thanks are due to Dr. K. Das Gupta for his valuable guidance and for introducing him to the technique. Thanks are also due to Dr. R. K. Datta Roy for his kind co-operation.

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