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EXTRA LiF(220) REFLECTIONS FROM HEAVY ELEMENT X-RADIATION

by

Dorothy J. Reed

MINERAL SCIENCES DIVISION

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INTRODUCTION

The narrow 2d spacing of the LiF(220) crystal coupled with the good reflectivity has made it attractive for the dispersion of K radiation of the heavy elements. The separation of neighbouring elements is almost as good as that of quartz (2d=2.74) and the counting rate is much higher: up to 90% of that of LiF(200) compared with 15% for quartz, although these percentages have been found to vary with the counting conditions used, as well as the samples.

The crystal suffers, however, from the occurrence of extra reflections for silver and the heavier elements. These can pose particular problems when X-ray spectrography is used to check the purity of specimens of heavy elements or when neighbouring elements occur in the same sample. The position and intensity of such extra reflections are reported in this paper. Their source within the crystal was not investigated because interest was centered on the analytical problems they presented. These arise from the presence of the peaks regardless of their origin.

OCCURRENCE OF EXTRA REFLECTIONS

When the characteristic radiation excited in a sample component has sufficient energy to penetrate to crystal planes not parallel to the surface of the analysing crystal, it may be reflected from them to reach the counter in significant amounts if the initial intensity is great enough. We have found such reflection to occur with our LiF(220) crystal for the K radiation of silver and the heavier elements.

Figure 1a reproduces a scan of tungsten powder at 88kV and 20mA which shows extra peaks A and B lying between the first-order WKα and second-order WKβ peaks. These peaks were called A and B for convenience, with B being used to designate the one with the higher energy because a relationship between these peaks and the characteristic radiations seemed a reasonable assumption.

These peaks can interfere with peaks of other elements or cause confusion by being mistaken for minor constituents, but they are broader than and lack the Gaussian symmetry of characteristic radiation.

Peaks also occur between the second and third orders of the characteristic radiation for cesium and the heavier elements. Those for hafnium are shown in Figure 1b which presents a scan of HfO_2 at 80kV and 20mA. The first-order A is also included in this figure. A third order of the extra reflections was not sought because of the low intensity that was expected and because, in many cases, there would be interference from the L lines of the tungsten X-ray tube target.

First-order extra reflections were found for silver and lead and eleven intervening elements in the periodic table - all of those scanned - while second-order became evident starting with cesium.

POSITION OF EXTRA REFLECTIONS

The positions of the extra peaks were determined for the elements used by making a count scan over them. The two-theta positions found for A and B were plotted against the atomic number of the source elements and resulted in smooth curves having the equation $Y = 43.2072 - 1.4648X + 0.01647X^2$ for A and $Y = 38.8342 - 1.3664X + 0.01593X^2$ for B, where X represents Z-40.

To validate the assumption that the extra reflections were those of the characteristic radiations reflected from deeper crystal planes, the two-theta angles of A for the various elements were plotted against the wavelengths of the corresponding Kα1 and of B against those of Kβ1.

All points lay on the same line. A similar line resulted when the second order reflections were plotted in the same way. These lines are shown in Figure 1c. The lower line has the equation $Y = 62.149236X - 0.3395$ and a correlation coefficient of + 0.9999. The equation for the upper line is $Y = 104.6662X - 0.5708$ and the correlation is the same as that of the lower.

From these lines the positions of the extra peaks for the intervening elements that might be of analytical interest in our laboratory were calculated. These are given in Table 1. They are also included in the Mines Branch Information Circular IC226 which is a compilation, calculated originally for our own use, of the two-theta values for LiF(220) for the lines of elements of analytical interest.

INTENSITY OF EXTRA REFLECTIONS

As further evidence of the relationship between the extra reflections and the characteristic ones, net intensities were determined for all the peaks. Table 2 compares the ratios $K\alpha/K\beta$ with A/B. With the exception of lanthanum, they show good agreement as long as the intensity of the extra peaks is sufficient to ensure significance of the counts, i.e., cesium and the heavier elements.

The ratios of $K\alpha$ to A and $K\beta$ to B are also presented in Table 2. Again there is a discrepancy for lanthanum and the elements lighter than cesium. The B peaks for these elements were so small that their estimation was difficult and these results are less reliable than the $K\alpha$/A ratios. All the ratios containing $K\beta$ for platinum and mercury are less reliable because the $K\beta$ peak was not completely resolved from the continuum - less so that W$K\beta$ in Figure 1a.

From Table 2 it can be readily calculated that the percentages of the extra peaks in terms of the characteristic ones are quite small. They range from 0.3 to 6.8% with increasing atomic number. The peaks may, therefore, be dismissed by some workers as insignificant. However, the A's are shown, in Figures 1a and b, to be larger than the characteristic $K\beta$'s of the next higher order.

TABLE 1

Two-Theta Values for the Extra Peaks Reflected from LiF(220)

Element		A	B	Element		A	B
Ag	47	34.48	30.42	Yb	70	14.39	12.60
Cd	48	32.96	29.07			24.21	21.31
In	49	31.54	27.80	Hf	72	13.48	11.80
Sn	50	30.20	26.61			22.66	19.76
Sb	51	28.94	25.48	Ta	73	13.06	11.46
Te	52	27.75	24.43			21.96	19.40
I	53	26.63	23.43	W	74	12.66	11.10
Cs	55	24.58	21.60			21.28	18.81
		41.39	36.25	Re	75	12.27	10.76
Ba	56	23.63	20.77			20.64	18.25
		39.79	34.87	Os	76	11.90	10.44
La	57	22.73	19.98			20.01	17.71
		38.28	33.55	Ir	77	11.54	10.12
Ce	58	21.88	19.22			19.42	17.18
		36.85	32.30	Pt	78	11.20	9.82
Pr	59	21.08	18.51			18.82	16.67
		35.48	31.10	Au	79	10.87	9.53
Nd	60	20.32	17.83			18.26	16.20
		34.20	29.99	Hg	80	10.55	9.26
Sm	62	18.88	16.59			17.73	15.74
		31.78	27.92	Tl	81	10.24	8.98
Gd	64	17.60	15.43			17.20	15.29
		29.93	26.00	Pb	82	9.94	8.73
Dy	66	16.43	14.39			16.70	14.87
		27.64	24.27				

TABLE 2

Ratios of Characteristic and Extra Peaks

Element		$K\alpha/K\beta$	A/B	KA/A	KB/B
Hg	80	3.78	3.50	14.24	13.17
Pt	78	3.36	3.56	20.38	21.62
W	74	3.90	3.92	14.70	14.81
Hf	72	3.68	3.83	14.78	15.30
Gd	64	3.36	3.40	17.68	17.79
Sm	62	3.29	3.16	17.97	17.36
Nd	60	3.55	3.56	23.12	23.52
La	57	3.15	2.70	28.00	24.00
Cs	55	3.78	3.78	40.34	40.16
Te	52	3.70	2.61	56.80	41.07
Sn	50	3.83	2.66	101.66	68.58
Ag	47	3.73	1.58	307.62	130.19

DR/pg

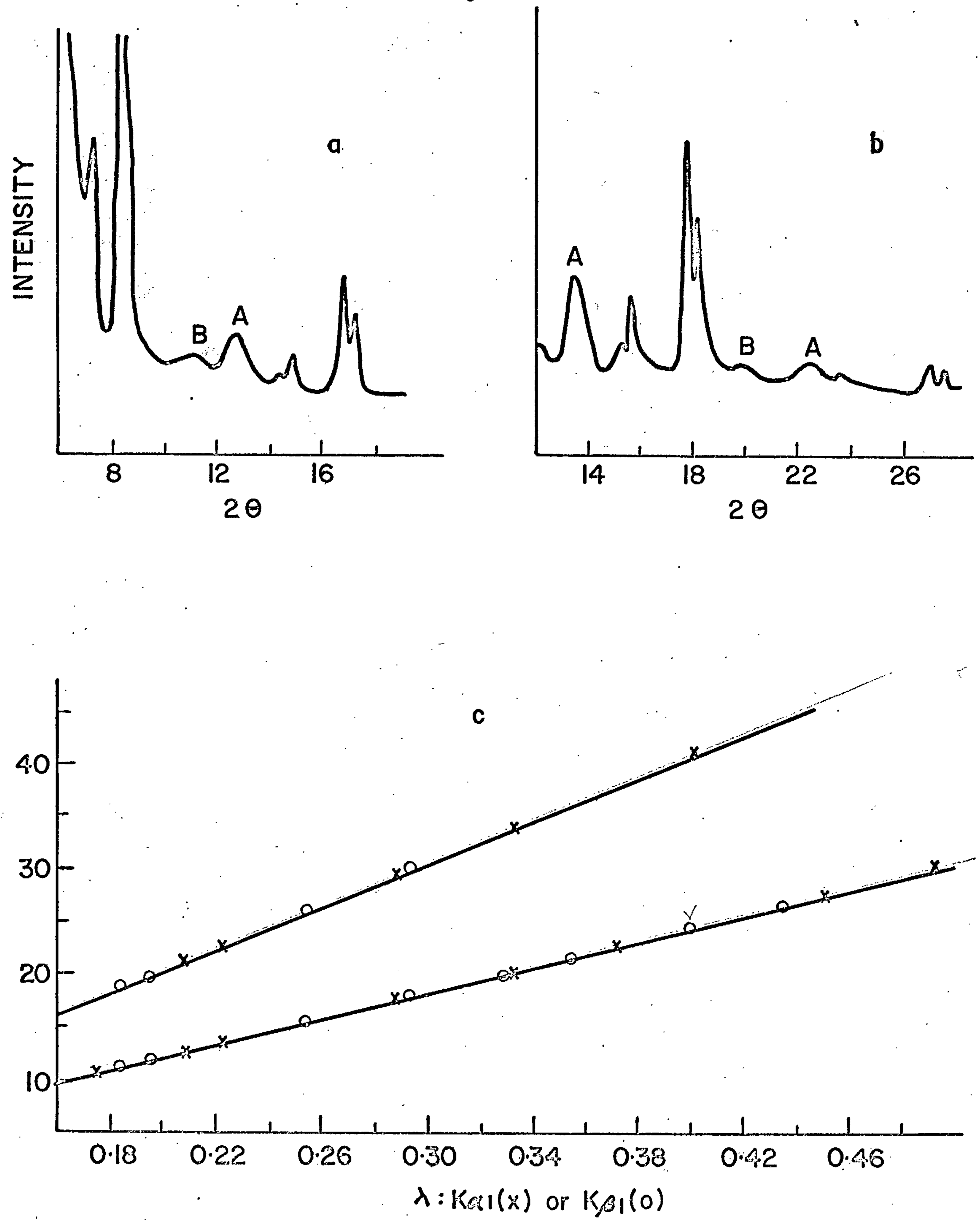

Figure 1. - Relationship of Extra Peaks to Characteristic Peaks.