Effects of Chemical Composition on X-Ray Lines

H. H. ROSEBERRY AND J. A. BEARDEN, *Rowland Physical Laboratory, Johns Hopkins University*

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The influence of chemical combination with oxygen on the width, index of asymmetry and separation and ratio of peak intensities of the alpha-doublet of the elements Ti, Cr, Mn, Fe and Zn of the K-series emission lines has been studied with a double crystal spectrometer. The widths of the alpha-lines were increased 3 to 35 percent and the beta-lines were increased 4 to 30 percent except in two cases, namely that of the $K\alpha_1$-line of TiO_2, whose width decreased 3 percent, and that of the beta-lines of the oxides of Mn, whose width remained the same as that of the pure metal. No effect of chemical composition on the widths of the gamma-lines was observed. The $\alpha_1 \rightarrow \alpha_2$ separations were unaffected by chemical composition. The asymmetries of all the lines were unaffected with the exceptions of the alpha-lines of TiO_2, and the $K\alpha_1$- and the beta-lines of MnO and Mn_3O_4. The ratios of peak intensities of the alpha-lines were affected by changes of width caused by chemical composition such that the ratio of areas remained 2 : 1.

INTRODUCTION

THE effects of chemical combination on x-ray emission spectra have been the subject of numerous investigations[1-18] in the past few years. The effects found so far are: changes in frequency,[1, 2, 8, 10, 11, 13] in relative intensity,[9] in width,[9, 12, 14, 15, 16] of certain emission lines, and in some cases the appearance of new lines.[9] All of this work, with two exceptions, has been done with vacuum photographic spectrometers, with indefinite conclusion due in the main to the lack of resolving power either in the spectrometer itself or in the microphotometer used to analyze the photographic plates. A double crystal spectrometer was used by Wilhelmy,[16] who found that the Cu $K\alpha_1$-line from CuF_2 was much wider than that from pure copper, and by Parratt,[14] who examined two ($K\alpha_1$ and $K\alpha_2$) of the much

studied sulphur lines. In none of the above cases have all the lines of a complete emission series been studied as a function of chemical combination under the same conditions of resolving power. In the present work the changes introduced in all the lines of the K-series (except Ti $K\gamma$) have been measured with a double crystal spectrometer for a number of substances sufficiently stable that they may be used satisfactorily as x-ray targets.

APPARATUS

Spectrometer

The double crystal spectrometer is of a precision type built by the Gaertner Scientific Corporation. The first crystal was mounted on a slide midway between the focal spot of the x-ray tube and the axis of the second crystal,[19] so that the wave-length region to be studied could be selected by simply adjusting the slide. The angular position of the second crystal was determined by reading the divided circle with two microscopes. Small displacements were measured by a worm-gear tangent screw and dial. Angular settings could be repeated with the tangent screw within 0.2 second of arc.

The ionization chamber was 6 cm in diameter, 13 cm long and made of steel to reduce alpha particle contamination.[20] The chamber was filled with pure argon at atmospheric pressure. The ionization current was measured by a Compton electrometer with a voltage sensitivity of 3 meters per volt. The peak of the weakest line measured

[1] Lindh and Lundquist, Ark. f. Matem. Astr. o. Fysik, Vol. 18, Nos. 14, 34, 35 (1924).

[2] Lundquist, Zeits. f. Physik **33**, 901 (1925); **60**, 642 (1930); **77**, 778 (1932); **89**, 273 (1934).

[3] Bäcklin, Zeits. f. Physik **33**, 547 (1925); **38**, 215 (1926).

[4] B. B. Ray, Phil. Mag. **49**, 168 (1925); **50**, 503 (1925).

[5] Ortner, Wien Sitzungsber. II a **135**, 71 (1925); **136**, 369 (1927).

[6] Wetterblad, Zeits. f. Physik **42**, 603 (1927).

[7] Owens and Williams, Proc. Roy. Soc. A**132**, 282 (1931).

[8] Faessler, Zeits. f. Physik **72**, 734 (1931).

[9] Deodhar, Proc. Roy. Soc. A**131**, 647 (1931).

[10] Svensson, Zeits. f. Physik **75**, 120 (1932).

[11] Valasek, Phys. Rev. **43**, 612 (1933); **47**, 896 (1935).

[12] Yoshida, Inst. Phys. Chem. Res. Tokyo Sci. Rep. **421**, 298 (1933).

[13] Tanaka and Okuno, Phys. Math. Soc. Japan Proc. **17**, 540 (1935).

[14] Parratt, Phys. Rev. **45**, 364 (1934); **49**, 14 (1936).

[15] Siegbahn and Magnusson, Zeits. f. Physik **96**, 1 (1935).

[16] Wilhelmy, Zeits. f. Physik **97**, 312 (1935).

[17] Shearer, Phil. Mag. **20**, 504 (1935).

[18] Johnson, Zeits. f. Physik **95**, 93 (1935).

[19] Ross, Phys. Rev. **39**, 550 (1932).

[20] Bearden, Rev. Sci. Inst. **4**, 271 (1933).

gave an ionization current of 10^{-14} ampere. The average deviation from the mean reading at the peak of the line did not exceed 0.5 percent for the majority of the lines and for the weakest lines was approximately 2 percent.

Crystals and slits

The crystals were split from a large sample of perfectly clear Iceland calcite. The freshly cleaved surfaces gave a rocking curve width for the copper $K\alpha$-lines (1.54A) of 10.8 seconds, which is 1.2 seconds greater than the theoretical value of 9.6 seconds.[21] The crystals were ground, polished and etched[22] and then gave 9.8 seconds width and a percentage reflection of 55 percent. The alignment of the crystals was effected as previously described[23] using the $K\alpha$-lines of copper and titanium in the $(1-1)$ and the $(1+1)$ positions. This method makes the atomic planes rather than the cleavage planes parallel.[23] The measured physical resolving power of these crystals for the Cu $K\alpha$-lines was 11,000 in the $(1+1)$ position.

The first slit was 1.0 mm high (vertical projection of the focal spot), the second slit 10.0 mm high and the separation of the slits was 55 cm, giving a geometrical resolving power of 40,000. Since the crystals were always used in the first order where the measured physical resolving power is 11,000, the effective resolving power was determined by the perfection of the crystals and not by the geometrical resolving power.

X-ray tube

The water-cooled target was permanently mounted in a vertical position and arranged so that the glass body of the tube could be lowered over the target and the ground joint between the glass and target made tight with Apiezon sealing compound. This arrangement made possible the change of target material without disturbing the target's alignment with the crystals of the spectrometer. The target was cut at an angle of 10° with the horizontal and the focal spot thus acted as the first height limiting slit for the spectrometer. It has previously been shown[24]

that satisfactory targets for accurate ionization chamber measurements can be made by pounding the desired material into the surface of the copper target. This method has proved entirely satisfactory for substances used in the present work.

In order that the source of x-rays be as constant as possible and that the oxides not be heated unnecessarily, the following procedure was adopted: the x-ray tube was assembled and connected to the diffusion pump. The tube (except the ground joint) was heated to about 500°C and then the target heated by bombardment to about 800°C. This process of alternately heating the glass and bombarding the target was repeated several times until the tube would operate with the target at 800°C without any evidence of gas. The tube was opened and the desired chemical or pure metal was quickly pounded into the surface of the target. The tube was re-assembled and evacuated. The previous baking-out process made it unnecessary to reheat the target. When the substance was properly pounded into the target the thermal contact was sufficient to prevent either noticeable heating or any chemical change of the target material with prolonged operation of the tube. As a further precaution against any decomposition, the power input to the tube was maintained at less than 50 watts except when measuring the gamma-lines, when about 350 watts were used.

The high voltage transformer was supplied with 60 cycle a.c. from a generator driven by a d.c. motor. The control arrangement which maintained the primary voltage constant to 0.1 percent has already been described.[25] The high voltage circuit was the balanced filament type[24] which corrects for changes of space charge, charges on the walls of the tube, and minute changes of pressure. Over a period of two or three hours the intensity was constant to better than one percent.

EXPERIMENTAL PROCEDURE

The procedure for obtaining the contours of the various lines was as follows: The alpha-lines were observed first, recording the ionization current every second of arc in the vicinity of the

[21] Parratt, Phys. Rev. 49, 280 (1936).
[22] Manning, Rev. Sci. Inst. 5, 316 (1934).
[23] Bearden and Roseberry, Phys. Rev. 48, 110 (1935).
[24] Bearden and Shaw, Phys. Rev. 48, 18 (1935). In all tables the numbers in parenthesis are taken from this paper.

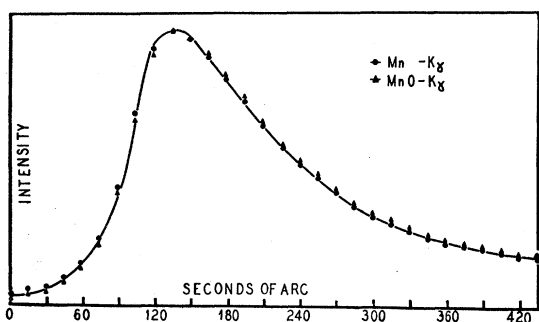[25] Bearden and Shaw, Rev. Sci. Inst. 5, 292 (1934).

FIG. 1. Mn $K\gamma$ from targets of pure Mn and MnO. The two curves corrected for the effect of the β-line are superimposed with peaks matched. The width and asymmetry of the γ-line are not affected by chemical composition.

FIG. 2. Mn $K\alpha$ doublet from targets of pure Mn and MnO. The two curves are superimposed with peaks matched. The widths of the $K\alpha_1$-lines of Mn and MnO are 76.5″ and 93.7″ respectively, and the corresponding widths of $K\alpha_2$ are 89.3″ and 97.5″. The indices of asymmetries of the $K\alpha_1$-lines of Mn and MnO are 1.54 and 1.42 respectively, and of $K\alpha_2$, 1.17 and 1.21.

peaks. Then observations were repeated several times near the region of half maximum and at the peak of the line so that the width and asymmetry could be accurately determined. The same procedure was followed in the case of the beta- and gamma-lines. Observations on the alpha-lines were made consecutively without any changes of voltage and current through the tube, hence the ratio of the two peak intensities could be secured. Similarly consecutive observations were made on the beta- and gamma-lines, and the intensity ratio of the two peaks obtained. No correction for differential absorption due to the window of the tube or air path was made to obtain this ratio.

After the complete K-series had been finished, the alpha-lines were repeated to see if any chemical changes of the target material had taken place. The maximum deviation from the values of the widths as recorded in Table I did not exceed one second, though the curves were
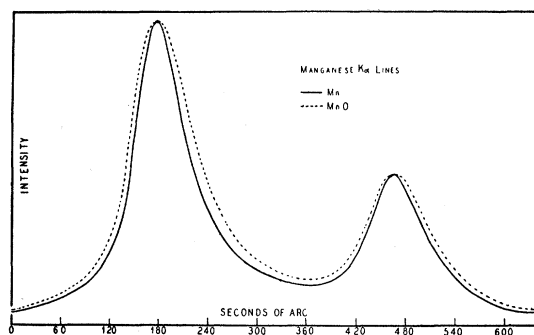
repeated after some 30 to 40 hours' operation of the tube.

The line widths and asymmetries of the K-series of the pure metals, copper, manganese, and titanium, were measured and found to be in excellent agreement with the results of Bearden and Shaw.[24] In the cases of iron, chromium, and zinc, new measurements were not made on the pure metals and the previous results[24] were used for comparison.

The base line of the alpha- and beta-lines was easily measured, and the widths, asymmetries and intensities were accurately determined. The base of the gamma-line had superposed upon it the foot of the intense beta-line. In the analysis of the gamma-line the following procedure was adopted. First, the curve for the pure metal and that of the compound were superimposed (with peaks matched) without any correction of base

TABLE I. *Effects of chemical composition on the widths of the emission lines of the K-series.*

Line........	$K\alpha_1$			$K\alpha_2$			$K\beta$			$K\gamma$		
Target......	Sec.	X.U.	Volts	Sec.	X.U.	Volts	Sec.	X.U.	Volts	Sec.	X.U.	Volts
Ti	80.9	1.06	1.74	109.3	1.43	2.34	109.8	1.46	2.87			
TiO$_2$	78.6	1.03	1.69	113.0	1.48	2.42	122.5	1.64	3.21			
Cr	(75.5)	1.03	2.43	(90.4)	1.23	2.90	(77.4)	1.07	3.05	(135.0)	1.86	5.38
Cr$_2$O$_3$	102.0	1.39	3.28	115.0	1.56	3.67	104.0	1.43	4.09	136.3	1.88	5.44
Mn	76.5	1.05	2.96	89.3	1.23	3.44	76.5	1.07	3.62	140.0	1.95	6.72
MnO	93.7	1.29	3.62	97.5	1.34	3.76	76.5	1.07	3.62	138.5	1.93	6.66
Mn$_3$O$_4$	100.2	1.38	3.88	103.3	1.42	3.98	76.3	1.06	3.61	140.0	1.95	6.72
Fe	(68.4)	.95	3.15	(80.1)	1.11	3.67	(73.2)	1.03	4.13	(119.0)	1.67	6.82
Fe$_2$O$_3$	85.2	1.18	3.92	84.8	1.18	3.88	85.2	1.19	4.81	118.5	1.66	6.79
Fe$_3$O$_4$	85.5	1.19	3.93	85.0	1.18	3.89	85.0	1.19	4.80	120.0	1.68	6.88
FeS	79.3	1.10	3.65	81.8	1.14	3.75	84.0	1.18	4.76	118.0	1.66	6.78
Zn	(36.9)	.527	3.18	(43.1)	.615	3.69	(63.5)	.911	6.73	(91.0)	1.30	9.83
ZnO	38.5	.549	3.32	42.6	.608	3.64	66.3	.951	7.03	92.0	1.32	9.91

TABLE II. *The effect of chemical composition on the indices of asymmetry and ratio of peak intensities.*

	INDEX OF ASYMMETRY				INTENSITY RATIOS	
	$K\alpha_1$	$K\alpha_2$	$K\beta$	$K\gamma$	α_1/α_2	β/γ
Ti	1.22	0.86	1.72		2.15	
TiO$_2$	1.01	1.00	1.76		2.43	
Cr	(1.37)	(1.03)	(1.53)	(2.54)	2.26[14]	
Cr$_2$O$_3$	1.36	1.03	1.54	2.58	1.92	40.1
Mn	1.54	1.17	1.37	2.35	2.20	50.0
MnO	1.42	1.21	1.75	2.36	2.16	52.1
Mn$_3$O$_4$	1.43	1.14	1.75	2.36	2.18	50.0
Fe	(1.61)	(1.26)	(1.75)	(2.44)	2.07[14]	
Fe$_2$O$_3$	1.61	1.24	1.79	2.46	1.85	32.9
Fe$_3$O$_4$	1.58	1.24	1.75	2.43	1.85	32.7
FeS	1.58	1.20	1.74	2.42	1.88	32.2
Zn	(1.12)	(1.33)	(1.48)	(3.02)	1.99[26]	
ZnO	1.12	1.33	1.46	3.05	1.74	34.4

TABLE III. *The alpha-doublet separation of the pure metals and their compounds.*

	Seconds	X.U.	$\Delta\lambda$ X.U.
Ti	139.5	3.65	
TiO$_2$	140.0	3.67	0.02
Cr	(143.0)	3.89	
Cr$_2$O$_3$	143.7	3.91	0.02
Mn	142.8	3.93	
MnO	143.5	3.96	0.03
Mn$_3$O$_4$	142.5	3.94	0.01
Fe	(141.2)	3.93	
Fe$_2$O$_3$	141.5	3.95	0.02
Fe$_3$O$_4$	141.7	3.95	0.02
FeS	141.2	3.93	0.00
Zn	(134.0)	3.82	
ZnO	133.7	3.81	0.01

line, to observe if the two contours fitted. The fit was in all cases within the error of observation. Second, the two curves were corrected for base line taking into account the effect of the beta-line, and third, as a final check, the two corrected curves were superimposed. The widths and asymmetries of the gamma-lines recorded in Table I are from the corrected curves. In Fig. 1 the corrected gamma curves of pure manganese and manganese oxide are superimposed showing how closely the two contours matched. In Fig. 2 the curves of the alpha-lines of pure manganese and manganese oxide are superimposed to illustrate the broadening due to chemical combination.

RESULTS
Widths of lines

There are recorded in Table I the effects of chemical composition on the full widths at half-maximum of the various lines of the K-series measured in the $(1+1)$ order. The alpha-lines are not resolved into components because of the uncertainty as to how this resolution is to be affected, since there is not sufficient information on the shapes of the individual lines for this purpose. In general, the alpha-lines showed the largest broadening effect, the beta-lines being considerably less influenced. The gamma-lines exhibited no change in width within an estimated observational error of five percent. This high observational error results from the difficulty in determining the base line accurately.

The data concerning the effect of chemical combination on asymmetry (the ratio of the

part of the full width at half maximum lying to the long wave-length side of the maximum ordinate to that on the short wave-length side) and the intensity ratios of the peaks of the various lines are given in Table II. The asymmetries of all the lines were unaffected with the exceptions of the alpha-lines of the TiO$_2$, and the $K\alpha_1$- and the beta-lines of MnO and Mn$_3$O$_4$. In both of these cases when the asymmetry of one line increases that of the other decreases.

Williams[26] has shown that in the present spectral region the correction to the intensity ratio $K\alpha_1$ to $K\alpha_2$ or $K\beta$ to $K\gamma$ for differential absorption in the target and windows is within the accuracy of observation; therefore no attempt was made to make these corrections. In the case of the beta to gamma intensity ratio which was secured from the corrected curves, no effect of chemical combination was observed. For the alpha-lines the ratio varied depending on the change of width involved; i.e., an increase of width was accompanied by a decrease of the intensity ratio, and *vice versa*. With the exceptions of the oxides of manganese this increase or decrease of the intensity ratio of the alpha-lines was very pronounced.

Alpha-doublet separation

The alpha-doublet separations obtained in the present work for the pure metals and their compounds are given in Table III. Because of the high resolving power of the double crystal spectrometer and the greater accuracy of the ionization method of recording the intensity distributions in wave-length, the doublet separa-

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[26] Williams, Phys. Rev. **44**, 146 (1933).

tion as obtained is more reliable than former data secured by photographic methods. The angular distance between the two peaks could be repeated with an accuracy of one second ($=0.03$ X.U.). Within this experimental deviation the separation of the alpha doublet was unaffected by chemical composition.

DISCUSSION

Titanium

The pure metal has a cubic crystal form and the oxide used (TiO_2, spectroscopically pure rutile) has a tetragonal crystal form. The results obtained in the case of TiO_2 were different from those found for the other chemical compounds, in that the $K\alpha_1$-line showed a *decrease* of width of 3 percent, while the $K\alpha_2$-line showed an *increase* of width of 3 percent, and the beta-line showed an increase of width of 11 percent. The indices of asymmetry for Ti $K\alpha_1$ for the pure metal and the oxide were respectively 1.22 and 1.01 and for Ti $K\alpha_2$ 0.86 and 1.00. Hence a decided effect of chemical composition is noted on the asymmetries of these lines.

Chromium

The pure metal has a cubic crystal form, while the crystal form of the oxide Cr_2O_3 is hexagonal. The $K\alpha_1$-line was broadened 35 percent, the $K\alpha_2$-line was broadened 27 percent, and the beta-line was broadened 34 percent. No effect was noted for the gamma-line, its width and asymmetry remaining the same as that for the pure metal.

Iron

The crystal forms of iron and Fe_3O_4 are cubic, and those of Fe_2O_3 and FeS are hexagonal. The $K\alpha_1$-lines of Fe_2O_3 and Fe_3O_4 were both broadened 25 percent, and the $K\alpha_1$-line of FeS was broadened 16 percent. The $K\alpha_2$-lines of the two oxides were broadened 6 percent and that of the sulfide 2 percent. The beta-lines of the oxides were broadened 16 percent, and that of the sulfide 14 percent. In the case of the lines of Fe_2O_3 and Fe_3O_4 where the same percent of broadening was experienced, there is represented an example in which the broadening of a line cannot be correlated with the crystal structure, for the crystal forms of these two oxides are different. The widths of the gamma-lines from the oxides and the sulfide remained the same as that of the pure metal within experimental error. No change of asymmetry was observed for any of the K-series lines.

Manganese

The crystal forms of the pure metal and MnO are cubic and Mn_3O_4 is tetragonal. The striking result in this case is that no broadening was observed for either the beta- or gamma-lines of any of the compounds. The $K\alpha_1$-line of MnO was broadened 22 percent and that of Mn_3O_4 30 percent. The $K\alpha_2$-line of MnO was broadened 9 percent and that of Mn_3O_4 was broadened 16 percent. The asymmetries of the $K\alpha_1$-lines of the oxides changed slightly but no effect was noted in the case of the other lines.

Zinc

The crystal form of the pure metal and that of the oxide are hexagonal. Only a small broadening of the lines was noted in this case. The $K\alpha_1$- and beta-lines broadened 4 percent and the $K\alpha_2$-line broadened 1 percent. The gamma-line was unaffected.

The question of just how atomic environment affects the energy states of the emitter and changes the widths of the lines as observed here is not obvious. In some way the lifetime of the excited state appears to be changed, but just why the electrons in the L-shell are those which are usually affected is not clear, when one would expect the electrons in the outer shells to be affected by chemical combination more than the internal electrons. Other factors which may need to be considered in framing a satisfactory theory are: the Auger effect, the role played by valence forces, the effect of field potentials on the energy levels, and the probability distributions for the different levels.