

Widths of X-Ray Lines from Alloy Targets

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The widths of the $K\alpha$ x-ray lines have been found to depend upon the physical or chemical state of the target. Several alloys of Ni, Fe, Mn, Cr and Ti have been used. The widths of the lines of element A when alloyed with element B may be increased or decreased, depending on element B . Targets of Mn-Ni show an approximately linear increase in the width of $K\alpha_1$ with relative increase of Ni, reaching, at 50-50 atomic concentration, a maximum width of 23 percent greater than the width from pure Mn,

then, with further addition of Ni, an approximately linear decrease with the same slope as before. In general the width of $K\alpha_1$ is more susceptible than of $K\alpha_2$ to changes in the atomic environment but the ratio of peak intensities varies in a compensating manner to allow the ratio of integrated intensities of α_1 to α_2 to remain constant, 2 to 1, within the estimated error of ± 4 percent. All the lines are asymmetrical.

IN the present study of the contour of the $K\alpha$ x-ray doublet a dependence of the line breadth and shape on the physical or chemical state of the emitting target has been observed. The widths of the lines of element A when alloyed with element B may be greater or less, depending on element B , than the widths of the lines of pure A . It seems possible that the effect is akin to the "pressure broadening" of lines in the optical region.

APPARATUS

The double-crystal vacuum spectrometer with which the ionization curves of these lines were taken has been previously described,¹ and the crystals, slits, method of recording readings, etc., discussed in an earlier paper.² The voltage with all the present targets was 15 kv and currents from 3 to 25 m.a.

With the removable target of the x-ray tube, the various alloy specimens of a given element were inserted without disturbing the settings or geometrical alignment of the instrument, thus allowing the rocking curves of the element in pure and in alloy states to be observed in more or less rapid and alternate succession. Since we are interested in comparing contours of lines of the same wave-length, the uncertain distortions due

to the instrument itself (crystals and slits) are constant and of little or no importance.

TARGETS

All the targets, except the Mn_2O_3 (?) and Ti-Si, were produced³ by an aluminothermic reduction from their oxides, thus assuring a relatively high degree of accuracy in their composition. The Mn_2O_3 was formed by oxidizing the surface of a pure Mn target by heating in air with a blow torch until a heavy layer of dark oxide had formed, probably a mixture of MnO, Mn_2O_3 and MnO_2 . After completing the curves the oxide layer was visually examined and found to be imperceptibly altered by the uncertain physical conditions of the focal spot. The Ti-Si was obtained commercially and is of unknown preparation.

Unless otherwise designated the alloy liquidus was allowed to cool in air in the clay crucible in which it was prepared. The pure Mn was slowly cooled in a large sand bed, giving supposedly the α -phase. The α -Fe (single crystal) was produced by very slow cooling over a period of 1000 hours, and the γ -phase, with a trace (about 2 percent) of carbon present, by quenching. After the γ specimen had been used as a target it was polished, etched with alcohol and HNO_3 , and

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¹ Parratt, *Phys. Rev.* **41**, 553 (1932).

² Parratt, *Phys. Rev.* **44**, 695 (1933).

³ The author is indebted to Mr. L. G. Hall, metallurgist of Ryerson Physical Laboratory, University of Chicago, for the preparation of most of the alloy specimens in this work.

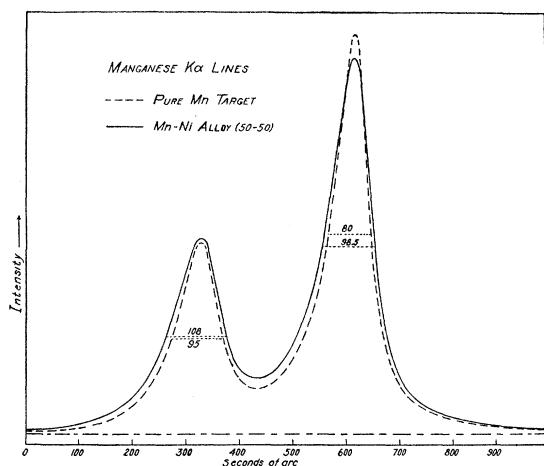


FIG. 1. Double-crystal ionization curves of the Mn $K\alpha$ doublet from targets of Mn-Ni alloy (50-50 atomic concentration) and pure Mn.

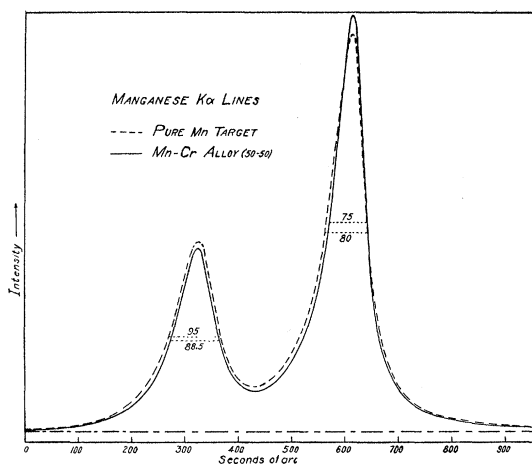


FIG. 2. Mn $K\alpha$ doublet from targets of Mn-Cr alloy and pure Mn.

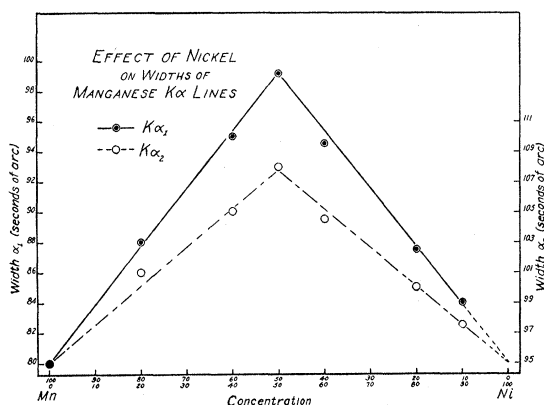


FIG. 3. Variations in widths of the Mn $K\alpha$ lines with concentration of Ni in Mn-Ni alloys.

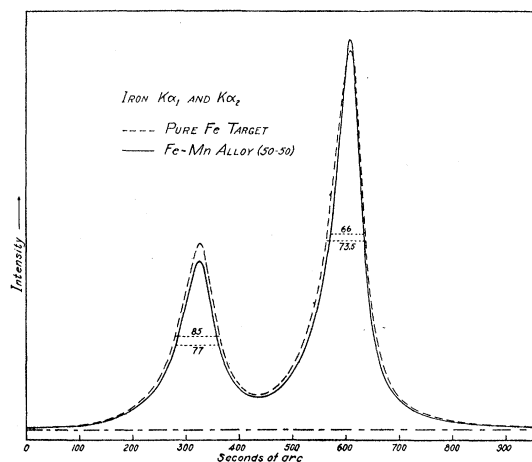


FIG. 4. Fe $K\alpha$ doublet from targets of Fe-Mn alloy and "pure" Fe.

microscopically examined. Both austenite, which is undercooled γ -Fe, and martensite, whose structure is now a controversial subject—possibly a strained α or a tetragonal lattice, were observed. Sufficient martensite was present to cause the sample to be ferromagnetic. We shall refer to this target as γ -Fe with the understanding that other forms of Fe were present and that the perturbing influence of the carbon on the x-ray line widths may not be negligible. Consequently, the data on " γ -Fe" in this paper should not be considered as quantitative except, perhaps, for the particular alloy specimen used.

The concentration ratio of the alloys refers to atomic concentrations except in the cases marked (wt) where the basis is that of weight.

RESULTS

In Table I are presented the data obtained from Mn (25) and several Mn alloys. Figs. 1 and 2 give curves of Mn alloys superposed on the curve of pure Mn, showing a relative increase and decrease in the breadth of each of the $K\alpha$ lines. For just one alloy, the Mn-Ni series,⁴ has the change in width been studied as a function of concentration. These data are shown in Fig. 3.

Measurements of the curves of pure Fe (26)

⁴ The alloy system of Mn-Ni is reported in the literature as a continuous series of solid solutions, but many systems so reported have been found by careful x-ray analyses to have more than one solid phase. It has been suggested that the structure of the Mn-Ni alloys is also more complex than previously assumed.

and of Fe alloys are listed in Table II. The change in the Fe $K\alpha$ doublet due to the presence of Mn is indicated in Fig. 4. The difference between the two allotropic forms of Fe, the α - and γ -structures, is felt to be greater than experimental error and introduces an ambiguity as to which form should be used, for purposes of comparison, as characteristic of Fe. Fig. 5 shows graphically the widths of both irons in relation to the widths of neighboring pure elements. In Fig. 4 the quenched or γ -Fe is arbitrarily taken as representing "pure" Fe for the reason that the lattice structure of the Fe-Mn alloy is that of γ -Fe, face-centered cubic. Supposedly the α -phase of Mn and Cr is the one present in the "pure" targets of each of these elements.

Table III gives the data from a few other alloys and Fig. 6 the perturbing influence of silicon on the titanium atoms.

Certainly one or more molecular layers of oxide had formed on most of these targets in the few minutes between the final cleaning, by filing, and the pumping out of the x-ray tube. The effect of this oxide is probably small in all cases except calcium which oxidizes rather readily. Consequently the widths of the $K\alpha$ lines of Ca given in Fig. 5 may include the effect of the oxygen. A

TABLE I. *Rocking curves of Mn $K\alpha$ lines not corrected for overlapping.*

Target	Full Width at Half Max.				Ratio of peak intensities α_1/α_2
	X. Units		Pure Mn taken as 1.00		
	α_1	α_2	α_1	α_2	
Mn pure annealed	1.10	1.31	1.00	1.00	2.15
Mn ₂ O ₃ (?) compound	1.27	1.46	1.15	1.12	2.10
Mn-Cu 30-70	1.30	1.45	1.18	1.11	2.00
Mn-Cr 50-50	1.03	1.22	0.94	0.93	2.17
Mn-Fe 50-50	1.15	1.33	1.05	1.02	2.13
Mn-Ni 80-20	1.21	1.39	1.10	1.06	2.05
Mn-Ni 60-40	1.31	1.45	1.19	1.11	2.00
Mn-Ni 50-50	1.36	1.49	1.23	1.14	1.98
Mn-Ni 40-60	1.30	1.44	1.18	1.10	2.06
Mn-Ni 20-80	1.21	1.38	1.09	1.05	2.07
Mn-Ni 10-90	1.16	1.34	1.05	1.03	2.13

slight amount of tungsten was sputtered on the targets from the filament of the tube but the effect of these foreign W atoms is probably negligible due to the relatively great average depth in the target at which the x-rays are generated.

The width of $K\alpha_1$ is, in general, more susceptible than that of $K\alpha_2$ to alterations in the atomic environment. In just one instance, that of the Ti-Si target, were the changes in widths of α_1 and α_2 of opposite sign. Except for the two pure

TABLE II. *Rocking curves of Fe $K\alpha$ lines not corrected for overlapping.*

Target	Full Width at Half Max.				Ratio of peak intensities α_1/α_2
	X. Units		γ -Fe taken as 1.00		
	α_1	α_2	α_1	α_2	
Fe quenched γ -Fe	1.02	1.18	1.00	1.00	2.07
Fe pure annealed α -Fe	1.06	1.23	1.04	1.04	2.17
Fe-Cr 50-50	1.00	1.15	0.98	0.98	2.05
Fe-Cr 40-60 (wt) annealed	1.01	1.17	0.99	0.99	2.09
FeAl ₂ compound	0.97	1.18	0.95	1.00	2.15
Fe-Mn 50-50	0.92	1.07	0.90	0.91	2.20
Fe-Ni 50-50	1.06	1.23	1.04	1.04	2.00
Fe-V 50-50	0.96	1.14	0.94	0.96	2.14

TABLE III. *Rocking curves of Ni, Cr and Ti $K\alpha$ lines not corrected for overlapping.*

Target	Full Width at Half Max.				Ratio of peak intensities α_1/α_2
	X. Units		Pure taken as 1.00		
	α_1	α_2	α_1	α_2	
Ni pure	0.71	0.91	1.00	1.00	2.30
Ni-Mn 40-60	0.77	0.97	1.07	1.06	2.32
Cr pure	1.09	1.40	1.00	1.00	2.26
Cr-Fe 60-40 (wt) annealed	1.11	1.43	1.02	1.02	2.15
Ti pure	1.24	1.58	1.00	1.00	2.19
Ti-Si 83-17 (wt) compound excess Ti	1.14	1.63	0.92	1.03	2.43

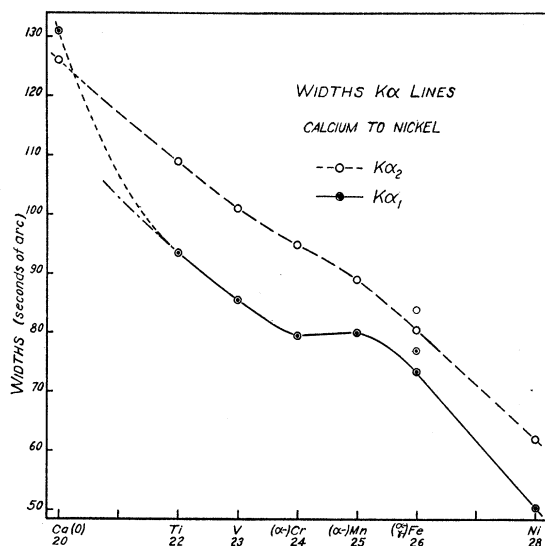


FIG. 5. Widths in seconds of arc of $K\alpha$ lines of pure elements. The two allotropic forms of Fe, α and γ , are given, the lower values those of γ -Fe. The α -phase of Cr and Mn is supposedly present in these two targets. An oxide layer on the surface of the Ca target may have an effect on the widths of the lines of Ca.

irons, a decrease in width is attended by an increase in the ratio of peak intensities⁵ and *vice versa*. This is to be expected in view of the relative changes in widths of α_1 and α_2 if the ratio of the integrated intensities of the two (component) lines be supposed constant.

An attempt has been made to resolve the observed overlapping curves into the two components, α_1 and α_2 , but the method is one of trial and error² since the components are asymmetrical and of different degrees of asymmetry. The ratio of the areas under the component curves may be defined as the ratio of intensities of the two lines, and this areal ratio, measured with a planimeter, remains constant irrespective of the alloy composition of the target within the error of drawing

⁵ The ratio of peak intensities as given in the tables is subject to several corrections one of which is the absorption of the x-rays in the target. As Williams (Phys. Rev. **44**, 146 (1933)) has shown this correction is usually very small, entirely negligible for the wave-length difference (4 X.U.) between α_1 and α_2 excited with tube voltage as low as 15 kv. With the Fe-Cr target, and a similar relation applies with a few other targets, the wave-length of Fe $K\alpha$ radiation is shorter than the wave-length corresponding to the K absorption limit of Cr. Consequently the absorption of Cr for the region of Fe $K\alpha_1$ and α_2 varies much more rapidly with wave-length than does the

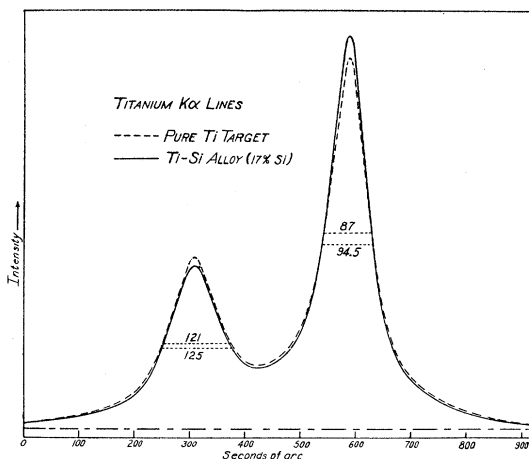


FIG. 6. Ti $K\alpha$ doublet from targets of Ti-Si alloy and pure Ti.

the component curves, estimated as less than 4 percent. The values of widths and peak intensity ratios listed in the tables are in description of the observed contours, uncorrected for overlapping.

There is a suggestion in the curves that the alterations in widths are not entirely symmetrical, possibly a greater effect being present on the long wave-length side. Part of this difference may lie in the error of superposing the alloy curves on those of the pure elements.⁶

The experimental error in the width measurements as estimated from the consistency of several curves for each target is less than ± 2 percent.

DISCUSSION

The information available in regards to the structures of alloy systems is as yet meager. Temperature equilibrium diagrams, many of them lacking in detail, of certain alloys and a few x-ray analyses of crystal structure comprise our knowledge to date.

absorption of Fe. However a simple calculation (after Williams) shows that the difference in the ratio of peak intensities due to the differential absorption of the Fe and Cr is less than the experimental error in the electrometer readings.

⁶ The wave-length of α_1 or α_2 (or the separation $\alpha_1 \rightarrow \alpha_2$) differed with alloying, if at all, by less than 0.14 X.U. or, in angular measure, by less than 10 seconds of arc. The spectrometer, because of the action of the stopcock grease in the bearings of axis B , would not repeat angular positions with certainty within this range of ± 5 seconds. Angular distances, however, could be repeated within 1 or 2 percent.

When two metals, *A* and *B*, are mixed together to form an alloy the atoms of *B* either replace atoms of *A* in the *A* lattice structure or enter the interspaces of the *A* lattice. When the atoms are more or less the same size, as is the case in most of the alloys considered in this paper, the former, the replacement process, is the one in effect, and the resultant lattice of *A* appears to be stretched or shrunk according, apparently, to whether atom *B* is greater or smaller than atom *A*. With further addition of atoms *B*, the limit of this homogeneous distortion of the *A* lattice may be reached, and, if so, the structure changes to that of another allotropic form of *A* or assumes the lattice of *B*. In the latter case the *A* atoms become the invaders. The region of concentration in which these lattice structures occur may overlap, with resultant mixed crystals. In case a definite compound of *A* and *B* is formed the picture can be somewhat more complicated by the addition of the third unit of structure, and much more so if a different type of internal binding is introduced. These relations have been ascertained⁷ directly by x-ray crystal analyses and, to a certain extent, may be inferred from the temperature equilibrium diagrams.

One of the characteristics of a metallic element is its apparent constancy of atomic volume, irrespective of the alloy structure. The atomic volumes of elements V to Cu are given in Table IV, calculated by Bernal⁸ from Goldschmidt's⁹ atomic radii.

TABLE IV. Atomic volumes ($\times 10^{-24}$).

V	Cr	Mn	Fe	Co	Ni	Cu
14.25	11.9	14.85	11.6	11.35	10.9	11.8

Mn-Cu¹⁰

The addition of Mn to Cu from 0 to 30 percent Mn increases the Cu lattice constant from 3.6 to 3.7A. Further additions of Mn cause the lattice of Cu to give way to that of Mn. The temperature equilibrium diagram of this alloy shows a strong

minimum at about 30 percent Mn, evidence, perhaps, that at this concentration the homogeneous distortion of the lattice is at its limit. For alloys not strictly isomorphous, the melting-point curve of the equilibrium diagram is of less importance than the changes in the solid phases. For example, at approximately 400°C the alloy of 30 percent Mn changes, upon further slow cooling, from the Cu lattice to that of β -Mn. The temperature of the emitting part of the target is of course unknown. The region of the focal spot as a whole is probably less than 400°C for this and most of the other targets concerned in this paper, but the neighborhood conditions of those individual atoms bearing the brunt of the enormous electron impacts are a matter of pure conjecture. No curves of the Cu $K\alpha$ doublet were taken for this target but the widths of the Mn lines are considerably increased as compared with the lines from pure α -Mn. No targets of pure β -Mn were attempted.

Mn-Fe¹¹

Alloys of from 40 to 60 percent Mn have the lattice of γ -Fe, face-centered cubic, with the lattice constant, at 50-50 concentration, 3.63 as compared with 3.58A for pure γ -Fe. No minimum is observed in the complex equilibrium diagram. The Fe lines are narrowed and the Mn lines broadened.

Mn-Ni^{4, 12}

There exists a greater difference between the atomic volumes of Mn and Ni than any other pair of metals studied. The equilibrium diagram shows a very marked minimum at approximately 50-50 concentration, very similar in form, when inverted, to the variations in the widths of the Mn lines, Fig. 3. Both the Mn and Ni lines are increased in widths.

α -Fe and γ -Fe

Goldschmidt¹³ has pointed out that a change in coordination number from 8 to 12, that is, a

⁷ *Strukturbericht*, 1913-1928, Zeits. f. Kristallographie.

⁸ Bernal, Trans. Faraday Soc. **25**, 367 (1929).

⁹ Goldschmidt, Trans. Faraday Soc. **25**, 253 (1929).

¹⁰ Patterson, Phys. Rev. **23**, 552 (1924); Persson, Zeits. f. physik. Chemie **9**, 25 (1930); Bain, Chem. Met. Eng. **28**, 21 (1923); Zemczuzny, Urasow and Rykowski, Zeits. f. anorgan. Chemie **57**, 253 (1908).

¹¹ Bain, reference 10; Ohman, Zeits. f. physik. Chemie **B8**, 81 (1930).

¹² Zemczuzny, Urasow and Rykowski, reference 10.

¹³ Goldschmidt, Zeits. f. physik. Chemie **133**, 397 (1928).

transformation of the α -lattice, body-centered cubic, into the γ -form, close-packed, is associated with an increase in the atomic diameter of about 3 percent. The lines from the more compact atoms of the α -Fe are wider than from the γ -structure.

Fe-Cr¹⁴

α -Fe and α -Cr have the same crystal lattice and very nearly equal atomic volumes. The Fe curves from the alloy are somewhat narrower than those from pure α -Fe, while the Cr lines are unaltered or slightly broadened.

Fe-Ni¹⁵

Over a large intermediate range of concentrations both the body- and face-centered Fe lattices are present, the relative amounts depending on the heat treatment. The equilibrium diagram is not simple, showing both a maximum and a minimum. The Fe and Ni atoms have similar atomic volumes. The widths of the Fe lines are the same as those obtained from pure γ -Fe.

¹⁴ Kreutzer, *Zeits. f. Physik* **48**, 556 (1928); Oberhoffer and Esser, *Stahl Eisen* **47**, 2021 (1927); Bain, reference 10.

¹⁵ McKeehan, *Phys. Rev.* **21**, 402 (1923); Bain, reference 10.

¹⁶ Asawa and Oya, *Sci. Rep. Tohoku Imp. Univ.* **18**, 727 (1929).

Fe-V¹⁶

The equilibrium diagram of this alloy system has a pronounced minimum, and there is a large difference in atomic volumes. Both elements have body-centered cubic crystals, and the narrowed Fe lines should perhaps be compared with the α -form of pure Fe.

The data are too fragmentary to permit explanations or correlations. Little is known of the forces involved in the metallic bond and even less as to the factors responsible for x-ray line widths. Just how the effects of alterations in the atomic environment, usually supposed to affect the outer or valence electrons only, can penetrate to the inner electrons involved in the $K\alpha$ -radiation is not obvious. Perhaps by changing the values of the energy levels by altering the field potential of certain atoms more than others due to their particular positions in the space lattice relative to the invading atoms. Perhaps by subdividing the energy states according to a Stark or Zeeman effect. Perhaps by altering the emission probability coefficients.

In conclusion the author expresses with pleasure his indebtedness to Professor S. K. Allison, Ryerson Physical Laboratory, University of Chicago, for the privileges of working in his laboratory where the data of this paper were taken.