THE CRYSTAL STRUCTURE OF IRON-NICKEL ALLOYS.

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ABSTRACT.

Crystal structure and density of a complete series of pure iron-nickel alloys. —Fourteen alloys were prepared by melting together Armco iron and electrolytic nickel, then swaging the castings and drawing and rolling into thin tapes. X-ray diffraction patterns were obtained with these, after various heat treatments. With from zero to 25 per cent Ni, the structure is chiefly body-centered-cubic, the parameter *a* increasing from 2.872×10^{-8} cm for *pure iron* to about 2.89×10^{-8} cm. With from zero to 70 per cent Fe, the structure is chiefly face-centered-cubic, the parameter *a* increasing from 3.510for *pure nickel* to about 3.60×10^{-8} cm. Around 30 per cent Ni, either structure is on the verge of instability and both or either may exist. Cold work tends slightly to increase the parameter. The densities of pure iron and nickel crystals come out 7.775 and 8.953 gm/cm³, respectively.

Speculations regarding atoms of iron and nickel.—It is probable that nickel atoms differ from iron atoms in possessing six electron orbits of a certain type in place of four. The behavior of these atoms in forming crystals is consistent with the idea that the directions of closest approach in either pure metal are the normals to the planes of these orbits and that in the intermediate directions, twelve for iron and eight for nickel, the atoms cannot approach so closely, these directions determining the positions of what we may call protuberances on the atoms. The electrons which are responsible for cohesion may be not the valence electrons but those in a deeper layer.

THE alloys of iron and nickel have long possessed great interest on account of the wide range in properties covered by the series and the irreversible character of certain of the transformations. No complete discussion of the alloys will here be attempted, only the results of X-ray crystal analysis being presented at this time. The method has been fully explained elsewhere, in connection with the analysis of certain alloys of silver with gold and palladium.¹ It should be stated here, however, that the experimental work on the nickel-iron series was practically completed before that on the noble metal series was commenced. The accuracy attained was not quite as high, partly on this account and partly on account of the more frequent occurrence of relatively large grains giving discrete spots in the film.

The qualitative work of Miss Andrews,² who found a transition in structure in the neighborhood of Fe(75)-Ni(25), from the body-centered cubic arrangement characteristic of Fe to the face-centered cubic arrange-

¹ L. W. McKeehan, Phys. Rev., 19, 537-538 (1922).

² Mary R. Andrews, Phys. Rev., 17, 261; 18, 245-254 (1921).

ment characteristic of Ni, is the only previous investigation in which a graded series of alloys reasonably free from impurities was used. In the present study the alloys used were made from Armco iron and electrolytic nickel melted together in a Northrup induction furnace, cast, swaged, drawn, and rolled into tape 0.015 cm thick. Chemical analyses of the castings showed that the desired compositions were nearly attained. For the X-ray analysis the tapes were further thinned by dipping in aqua regia, the best thickness being about 0.004 cm. This form of sample is well adapted to high accuracy where, as in the present case, large crystals do not occur.¹ Besides end members in this tape form, iron and nickel powders of high purity were available and were examined, packed in thin capillary glass tubes.

Three conditions were investigated for most of the samples; the first (I) was without preliminary heat treatment, the metal having been last previously passed several times through cold rolls; the second (2) was after a short anneal at 900°–950° C (except as noted) followed by slow cooling in the electric resistance furnace; and the third (3) was after a further heating to about 600° C followed by rapid cooling in air on a cold copper plate. A few of the samples were also analyzed in a fourth condition (4) obtained by chilling after (2) in liquid air for an hour or more. In Table I. are recorded the parameters a of the space lattices present, the per cent of nickel found by chemical analysis, the mean distance between the nearest atom-centers and the density ρ , computed by means of the following constants:²

Atomic weight of Fe	55.84
Atomic weight of Ni	58.68
Number of molecules per gram-molecule	6.0594×10^{23}
Wave-length of molybdenum $K\alpha_1$	$0.70783 \times 10^{-8} \mathrm{cm}$
$K \alpha_2 \ldots \ldots \ldots$	$0.71212 \times 10^{-8} \text{ cm}$

The results are given graphically in Fig. 1, which shows the variation in the parameters with the atomic composition which is given in the fourth column of Table I.

The increase in the face-centered cubic space-lattice parameter of nickel due to substitution of iron is evident, although not nearly so striking as the corresponding increase in other cases since studied.³ The increase in the body-centered cubic space-lattice of iron due to substitution of nickel is just appreciable in the short range of stability of this

¹L. W. McKeehan, Frank. Inst. J., 193, 231-242 (1922).

² L. W. McKeehan, Science 56, 754 (Dec. 29, 1922).

³ L. W. McKeehan, Phys. Rev., **19**, 537–538; **20**, 424 (1922). E. C. Bain, preprint No. 1139-N. Issued with Mining and Metallurgy (February, 1922); Chem. and Met. Eng. **28**, 21 (Jan. 3, 1923).

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space-lattice. The parameter for iron agrees with that found by others,¹ but that for nickel is less.² In the latter connection it is easy to see that high values would result from most of the probable impurities. The interesting changes in crystal structure in alloys with about 30 per cent Ni were noted by Miss Andrews.² This region is one of great variability in space-lattice parameter, and two reasons are suggested for this fact.



Either arrangement is on the verge of instability and correspondingly sensitive to small variations in composition or treatment, to the presence of impurities, and to similar causes. It is also possible for both phases to coexist, probably metastably, and there may be a certain degree of segregation of iron and nickel in such cases. The variability at the nickel end of the series may be attributed to impurities in the electrolytic nickel, which contained about half a per cent of other metals.

The general effect of cold-work is seen to be an increase of the parameters, due no doubt to incipient rupture in many of the crystals. The increase in crystal size due to annealing below the A_3 , $(\alpha - \gamma)$ transformation is very apparent in the photographs. This transformation occurs over a very wide range in temperature in passing from pure iron to a little past 30 per cent Ni³ and cannot be detected in these experiments at

¹ A. W. Hull, Phys. Rev., 10, 661–696 (1917). A. Westgren, Nature, 109, 817–818 (1922).

² A. W. Hull, Phys. Rev., 17, 571–588 (1922).

⁸ F. Hegg, Arch. des Sciences, 29, 592-617; 30, 15-45 (1910).

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34 per cent Ni (atomic). Since positive errors are more probable than negative the lowest point in each vertical group is generally to be preferred.

The distances between adjacent atom-centers vary, of course, in the same way as the space-lattice parameters, but the small difference between the values obtained in the two types of space-lattice shows how nearly it is permissible to consider the atoms as spheres. While the idea is highly artificial it may be worth noting that the effect of diluting either pure metal with the other is the same as if the iron and nickel atoms were equal spheres, with, respectively, twelve and eight symmetrically distributed protuberances. In the body-centered cubic arrangement of such iron atoms, the protuberances would not lie on the lines joining adjacent atom-centers, and the parameter of the space-lattice

Nominal Per Cent.		Ac- tual Per Cent.	Atom- ic Per Cent.	Condi- tion.	Body-centered cubic.			Fac	Note		
Fe.	Ni.	Ni.	Ni.		a.	$\Big \frac{1}{2} a_V \overline{\mathfrak{Z}}.$	ρ.	<i>a</i> .	$\left \frac{1}{2}a\sqrt{2}\right $	ρ.	
100	о			2	2.872	2.488	7.775				(a)
100	0	0.15	0.14	I 2 2 3	2.881 2.872 2.864 2.870	2.495 2.487 2.480 2.485	7.704 7.779 7.848 7.796	(3.629	2.566	7.712)	(b)
90	10	10.68	10.20	I 2 2 3	2.885 2.873 2.888 2.875	2.498 2.488 2.502 2.490	7.718 7.809 7.687 7.798	(3.586	2.536	8.034)	(b)
75	25	25.85	24.91	I 2 2 4 4	2.897 (2.902 2.874 2.880 2.877 2.887	2.509 2.513 2.489 2.494 2.492 2.501	7.676 7.636) 7.863 7.816 7.836 7.752	3.591 (3.608 (3.612 (3.604	2.539 2.552 2.554 2.549	8.062 7.944) 7.918) 7.966)	$(b) \\ (b) \\ (b, c) \\ (b) \end{cases}$
70	30	30.15	29.11	I 2 4 4	2.875 2.885	2.490 2.498	7.868 7.787	3.595 3.587 3.597 (3.600 (3.618	2.542 2.536 2.543 2.546 2.558	8.050 8.103 8.036 8.014) 7.898)	$(c) \\ (b) \\ (b)$
65	35	35.14	34.02	I 2 3				3.595 3.593 3.607	2.542 2.540 2.550	8.069 8.085 7.991	
55	45	45.57	44.35	I 2 3				3.602 3.588 3.594	2.547 2.537 2.542	8.063 8.163 8.117	

TABLE I.

Nominal Per Cent.		Ac- tual Per Cent.	Atom- ic Per Cent.	Condi- tion.	Body-centered cubic.			Face-centered cubic.			Note.
Fe.	Ni.	Ni.	Ni.		a.	$\frac{1}{2}a\sqrt{3}.$	ρ.	a.	$\frac{1}{2}a\sqrt{2}$.	ρ.	
45	55	55.82	54.61	I 2 3				3.586 3.581 3.569	2.535 2.532 2.524	8.217 8.245 8.330	
35	65	64.82	63.70	I I 2 3				3.569 3.574 3.582 3.579	2.524 2.527 2.533 2.531	8.371 8.335 8.279 8.301	
30	70	69.60	68.54	1 2 3		, î		3.571 3.570 3.562	2.525 2.525 2.519	8.374 8.381 8.441	
25	75	74.51	73.76	1 2 3				3.567 3.555 3.554	2,522 2,514 2,513	8.424 8.510 8.508	
21	79	78.54	77.69	1 2 3	-			3.569 3.566 3.564	2.524 2.522 2.520	8.429 8.446 8.465	
15	85	84.48	83.83	1 2 3				3.550 3.542 3.539	2.511 2.505 2.502	8.586 8.647 8.672	
5	95	94.24	93.96	1 2 3	*			3.531 3.543 3.528	2.497 2.505 2.495	8.774 8.682 8.795	
0	100	99.50	99.47	1 2 3				3.539 3.527 3.535	2.503 2.494 2.500	8.736 8.824 8.765	
0	100			2				3.510	2.482	8.953	(a)

TABLE I (continued).

Notes: (a) Pure powdered metals, glowed in reducing atmosphere.

(b) Values in parentheses due to few and faint lines.

(c) Annealing temperature 700° C in place of 900°–950° C.

would be the same as if the protuberances did not exist, but nickel atoms substituted for any of the iron atoms must present protuberances to some or all of its neighbors and thus distend the space-lattice. The same argument would explain the effect of iron atoms upon the space-lattice of nickel, and the effect would here be more positive because the packing is already closer, with less room for interatomic adjustment. The atomic number of iron is 26, that of nickel 28, so that there are two more electrons in the latter than in the former. If the crystal is held together by forces acting along the lines joining adjacent atoms, it is perhaps permissible to regard the eight neighbors of each iron atom as attracted by the eight faces of four elliptical electronic orbits, and the twelve neighbors of each nickel atom by the twelve faces of six elliptical electronic orbits. The twelve symmetrically arranged directions farthest from the eight bonds in the case of iron, the eight symmetrically arranged directions farthest from the twelve bonds in the case of nickel would correspond to the protuberances in the more mechanical picture first suggested.

It is suggested that the electrons responsible for the cohesion of metallic crystals are not the so-called valence electrons but those of a deeper layer relatively more firmly attached to the nucleus, the external electrons being left free in the sense required for electrical conductivity. We are already accustomed to the idea that nominally external electrons may penetrate into nominally internal layers so this idea is not at all revolutionary. The comparative weakness of metal crystals would be a natural consequence of this less intimate connection between adjacent atoms which would thus form a transition stage between valence-held salt-like crystals and amorphous liquids.

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