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KAMACITE AND TAENITE SUPERSTRUCTURES AND A METASTABLE TETRAGONAL PHASE IN IRON METEORITES

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Abstract

Kamacite and taenite in iron meteorites have cubic superstructures in which the unit cell edges are respectively three times and two times those of the disordered phases. Certain iron meterorites also contain a tetragonal phase that seemingly has the same chemical composition as kamacite. This is considered to be a transitional state in the transformation of γ-phase alloy into α-phase alloy (kamacite).

Introduction

X-ray powder photographs have been obtained from the iron-nickel phases in a number of iron meteorites. The meteorites examined include hexahedrites, octahedrites and nickel-rich ataxites (Table 1) in the form of polished slices that are currently the subject of microscopic investigations. For x-ray analysis each specimen has been sampled in two ways:

1. by gently scratching the surface with a biological needle;
2. by drilling powder from the surface with a tungsten carbide bur.

The first method yields a minute sample that can be mounted on the tip of a gelatin fiber, following the method of Sorem (1960). Samples of this type have been x-rayed in a 114.6 mm diameter camera using FeKα radiation and exposures of about 72 hours. The second method yields a considerably larger sample that can be mounted on a glass fiber using collodion as adhesive. Samples of this type have been x-rayed in a 114.6 mm diameter camera using FeKα radiation and exposures of about 8 hours. In both cases the x-ray film has been mounted according to the Ievins-Straumanis (asymmetric) method.

The powder patterns obtained from scratch samples differ considerably from those obtained from drilled samples of the same meteorite. Whereas the drilled samples yielded the simple cubic patterns of kamacite (α Fe-Ni alloy) and/or taenite (γ Fe-Ni alloy), the scratch samples yielded complex patterns containing many lines.

Analysis of the complex patterns has indicated

(1) the existence of a metastable tetragonal phase having the same composition as kamacite and (2) the presence of kamacite and taenite superstructures in which the unit cell edges are respectively three times and two times larger than those of the drilled samples.

These superstructures and the tetragonal phase are lost when powder is drilled from the meteorites.

Previous Work

Relatively little attention has been devoted to x-ray analysis of iron meteorites. Young (1926) x-rayed polished areas of kamacite and taenite in the Carlton meteorite and established that kamacite is body-centered cubic (like α-iron) and that taenite is face-centered cubic. He also established that the Widmanstätten orientation of kamacite in taenite is due to the development of the (110) planes of kamacite parallel to the (111) planes of the taenite. Derge and Kommel (1937) extended these studies of orientation in iron meteorites by using back reflection Laue photographs.

Table 1. Iron Meteorites Examined in this Study

Meteorite	Type	Symbol	Bulk Nickel Content %	Reference
Union	Hexahedrite	(H)	5.63	Henderson (1941)
Hex River Mountain	Hexahedrite	(H)	5.68	Cohen (1905)
Horse Creek	Hexahedrite	(H)	5.86	Goldberg, Uchiyama and Brown (1951)
Linwood	Coarsest octahedrite	(Ogg)	5.98	Henderson and Perry (1949)
			6.64	Goldberg, Uchiyama and Brown (1951)
Bischtübe	Coarse octahedrite	(Og)	6.48	Cohen (1897)
Mesa Verde Park	Medium octahedrite	(Om)	?	
Carlton	Fine octahedrite	(Of)	12.77	Howell (1890)
			12.68	Goldberg, Uchiyama and Brown (1951)
Linville	Nickel-rich ataxite	(D)	16.32	Cohen (1898)
Twin City	Nickel-rich ataxite	(D)	29.91	Mason (1962)

Owen and Burns (1939) were unable to prepare synthetic iron-nickel alloys that were rich in iron and in a state of complete thermal equilibrium. For this reason they x-rayed a number of iron meteorites in the hope that this would furnish information concerning the equilibrium conditions in iron-nickel alloys generally. The specimens used were filed from the meteorites and the powders annealed at 330° C. in order to obtain sharp x-ray reflections. The x-ray films showed only the simple patterns of kamacite and/or taenite. For comparison, they also x-rayed unannealed powders. These yielded the same spectra except that the lines were badly defined due to distortion of the metal.

More recently, Stulov (1960) has x-rayed a number of iron meteorites and has reported the existence of superlattice reflections in all of them. Unfortunately, Stulov used unfiltered iron radiation and also added sodium chloride to the powders to serve as an internal standard. As a result, the multiplicity of lines obtained (both α and β reflections being present) make the data difficult to interpret without ambiguity.

Stulov assigned indices to the observed superlattice reflections but does not discuss these results beyond mentioning that they could be due to ordering. However, on the basis of the indices given, the supercell would appear to have a unit cell twice that of kamacite. The existence of superlattice reflections in these samples is rather surprising in view of the fact that the specimens were obtained by drilling or filing powder from the meteorites. However, examination of Stulov's results shows that only four such reflections are identified and that generally only one of them (200), is present together with at most one other line. Hence it would seem that the powders contain only a fragmentary record of the original ordering.

The Tetragonal Phase

Evidence for a tetragonal phase. The evidence for a tetragonal phase appears only in the x-ray powder patterns of scratch samples; it is absent from the corresponding drilled samples. The structure was first recognized after comparing the d-values obtained from the Union and Horse Creek meteorites. The powder pattern of the Union meteorite contains 26 lines, four of which have d-values that correspond to the (110), (200), (211) and (220) reflections of kamacite. These reflections, however, are weak. The powder pattern of the Horse Creek meteorite contains 25 lines, none of which belong to kamacite.

A comparison of the two patterns shows that 18 of the unknown lines in the Union meteorite match 19 of the lines in the Horse Creek meteorite, one of the latter being an $\alpha_1\alpha_2$ doublet. Furthermore, the lines in common can all be indexed on the basis of a tetragonal unit cell, but not on the basis of a cubic or hexagonal unit cell. Examination of the powder patterns from all of the iron meteorites studied shows that this tetragonal pattern appears in six of the nine scratch samples but is absent from all the drilled samples. The three scratch samples that do not show this pattern are from the two nickel-rich ataxites (Linville and Twin City) and from the Hex River Mountain hexahedrite.

The d-values of the tetragonal phase are summarized in Table 2. Cell dimensions have been determined for the Union, Horse Creek, Bischtübe and Carlton meteorites and are approximately as follows:

	a(Å)	c(Å)	c/a
Union	7.12	5.70	0.80
Horse Creek	7.16	5.81	0.82
Bischtübe	7.16	5.74	0.80
Carlton	7.10	5.73	0.81

TABLE 2. d-VALUES OF THE TETRAGONAL PHASE

	Horse Creek (H)			Union (H)			Linwood (Ogg)		Bischtübe (Og)			Mesa Verde Park (Om)		Carlton (Of)		
hkl	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}
100	7.161	7.175	100	7.123	7.133	100	7.175	100	7.159	7.164	100	7.122	100	7.096	7.086	90
001	5.811	6.745?	1	5.696	[2]		[2]		5.739	[2]		[2]		5.733	[2]	
101	4.512	4.139	100	4.455	4.139	90	—	—	4.483	4.148	40	4.140	100	4.466	4.139	60
111	3.814	3.711	1	3.769	3.711	40	—	—	3.797	3.726	15	3.733	15	3.777	3.725	10
200	3.581	3.568	100	3.560	3.574	100	—	—	3.576	3.574	90	3.581	90	3.556	3.568	60
002	2.905	2.904[1]	15	2.849	2.849[1]	75	2.900[1]	15	2.870	2.870[1]	15	too faint		2.869	too faint	
220	2.531	2.562	70	2.517	2.549	60	—	—	2.529	2.563	15	2.556	10	2.508	2.562	15
112	2.522	2.493	70	2.479	2.497	60	—	—	2.496	2.490	15	2.496	10	2.490	2.490	40
300	2.386	2.392	10	2.375	2.380	5	—	—	—	—	—	2.386	1	—	—	—
221	2.322	2.340	60	2.305	2.334	60	—	—	2.315	2.340	15	2.340	15	2.300	2.340	10
310	2.262	2.295	10	2.251	2.285	10	—	—	2.265	2.293	10	2.301	10	2.243	2.301	1
400	1.791	1.790	1	1.781	1.781	5	—	—	1.790	1.790	1	1.787	1	1.774	1.774	40
411	1.664	1.667	15	1.653	1.659	10	1.670	5	1.662	1.664	1	1.670	1	1.647	1.682	10
213	1.657	1.622	1	1.631	1.622	1	—	—	—	—	—	—	—	1.638	—	—
114	1.396	1.376	70	1.374	1.376	5	—	—	1.381	1.376	75	—	—	1.379	1.376	70
214	1.321	1.304	70	1.303	1.305	1	—	—	—	—	—	—	—	—	—	—
324	1.172	1.148	100	1.157	1.148	10	—	—	1.162	1.148	100	—	—	1.165	1.148	100
		1.088α_1	80													
523	1.096			1.108	1.088	5	—	—	1.090	1.090	90	—	—	1.083	1.090	100
		1.082α_2	80													

[1] Broad line.

[2] This line is present but cannot be measured due to the darkness of the film.

Note: Only those lines which index in terms of the tetragonal cell are listed in this table. A number of large discrepancies between d_{obs} and d_{calc} are the results of errors made when measuring the position of the lines. These errors arise when it is difficult to distinguish the line from the background as is the case when 1) the line is very faint or 2) the line occurs at low 2θ where the film has been darkened as a result of long exposure to the x-radiation.

Composition of the tetragonal phase. Microscopic examination of the meteorites in reflected light has failed to reveal a discrete phase responsible for the tetragonal pattern in the x-ray films. In particular, the hexahedrites appear to have a uniform matrix that looks like kamacite. There is no obvious reason why the tetragonal pattern should appear in the x-ray film of the Union meteorite and not in that of the Hex River Mountain meteorite. Both are hexahedrites that look very much alike under the microscope. Modal analysis indicates that they contain similar amounts of rhabdite, (3.0 vol% in the Hex River Mountain meteorite, and 3.8 vol% in the Union meteorite), and according to Henderson (1941), both meteorites have essentially the the same chemical composition, *viz.*:

	Fe	Ni	Co	P	S	Cr
Union	93.09	5.63	nd	nd		
Hex River Mountain	93.59	5.68	0.66	0.25	0.08	0.02

Nevertheless, the x-ray pattern of the Union meteorite is tetragonal with only faint lines attributable to kamacite, whereas the x-ray pattern of the Hex River Mountain is cubic and wholly attributable to kamacite. It would seem, therefore, that the tetragonal phase in the Union meteorite has the same chemical composition as the kamacite in the Hex River Mountain.

Origin of the tetragonal phase. Recent work by Takashi and Bassett (1964), Clendenen and Drickamer (1964) and Bundy (1965) has demonstrated the existence of a high pressure hexagonal polymorph of iron known as ϵ-iron. The x-ray data for ϵ-iron (Takashi and Bassett, 1964) show no correlation with x-ray lines observed in the present study. Moreover, the present data cannot be indexed in terms of a hexagonal unit cell whereas all the lines can be indexed on the basis of a tetragonal unit cell. It is concluded, therefore, that the structure reported here is not related to a high pressure ϵ-type structure, but is a tetragonal phase.

Kamacite and the tetragonal phase cannot be distinguished under the microscope and they seem to have essentially the same composition. Furthermore, the tetragonal phase is metastable and converts to kamacite when subjected to the heat and stresses of drilling (Table 5). The absence of the tetragonal pattern in the x-ray films of the nickel-rich ataxites (Linville and Twin City) and, more especially, of the Hex River Mountain hexahedrite, indicates that this structure is not produced by scratching the meteorites but is a true property of the meteorite surface. It is suggested therefore that the tetragonal phase is an intermediate stage in the transformation of γ-phase into the α-phase (kamacite), and that it is able to coexist with kamacite of the same composition only because of the extremely sluggish approach to equilibrium exhibited in the Fe-Ni system. Such cubic-to-cubic transformations by way of a tetragonal transition structure are known to metallurgists, (see for example Smoluchowski *et al.*, 1951), but they have not been reported for iron-nickel alloys.

It is of interest to note that in the unit cell of the tetragonal phase the c repeat is essentially twice the unit cell edge of the corresponding kamacite to which it transforms in the drilled sample. For example, in the Carlton meteorite $c_{tet} = 5.73$ Å and the cell edge of the corresponding drilled kamacite is 2.869_8 Å. Since kamacite and taenite superstructures are identified in the present work, this relationship suggests that the tetragonal phase also may be a superstructure in which the dimensions of the supercell are double those of the disordered state. Assuming this to be true, then it can be seen that, in the absence of the superstructure, the disordered tetragonal phase would have one dimension, (the c repeat), the same length as the unit cell edge of the, presumably disordered, kamacite to which it transforms in the drilled powder. This is strong support for the proposition that it is a transitional stage in the γ-α transformation. Differences in cooling history might account for the preservation of this phase in some meteorites and its absence in others.

The Taenite Superstructure

Evidence for a taenite superstructure. The evidence for a taenite superstructure appears only in the x-ray powder patterns of scratch samples; it is absent from the corresponding drilled samples. The evidence is best documented in the patterns from the two nickel-rich ataxites Linville and Twin City.

The scratch powder pattern of the Twin City meteorite contains 13 lines, nine of which index on the basis of a cubic unit cell with edge (A) approximately 7.168 Å (Table 3). The four remaining reflections can be assigned to a body-centered cubic kamacite cell, one of the lines being a supercell reflection (Table 4). The drilled sample yields a pattern containing only nine lines (Table 5), five of which belong to a face-centered cubic taenite in which the cell edge (a) is approximately 3.582 Å, and four of which belong to a body-centered cubic kamacite the cell edge of which could could not be determined. It is clear that the unit cell edge of the taenite in the drilled sample (presumably disordered) is half that of the taenite in the scratched sample.

The scratch powder pattern of the Linville meteorite is particularly complicated and contains 46 measurable lines. Yet, all of these can be indexed on the basis of a taenite supercell with $A = 2a$ and a kamacite

TABLE 3. d-VALUES OF THE TAENITE

hkl	Twin City (D)			Linville (D)		
	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}
100?	7.168	7.050[1]	15	—	—	—
110	—	—	—	5.055	4.831	1
111	—	—	—	4.127	4.239	60
200?	3.584	3.516[1]	15	—	—	—
210	—	—	—	3.198	3.340	100
211	2.927	2.841	15	2.918	2.879	80
220	—	—	—	2.527	2.526	80
221	—	—	—	2.382	2.398	1
310	—	—	—	2.255	2.279	10
311	—	—	—	2.150	2.187	10
222	2.065	2.070	100	2.058	2.070	10
320	—	—	—	1.983	1.981	1
321	—	—	—	1.915	1.910	1
400	1.792	1.790	15	1.786	1.784	10
330	—	—	—	1.685	1.673	1
420	—	—	—	1.598	1.614	10
421	—	—	—	1.560	1.572	1
332	—	—	—	1.524	1.542	10
511	—	—	—	1.375	1.374	1
440	1.265	1.266	15	1.264	1.266	1
522	—	—	—	1.245	1.256	1
433	—	—	—	1.226	1.229	1
531	—	—	—	1.208	1.208	1
533	—	—	—	1.090	1.092	1
622	1.078	1.080	15	1.077	$1.081\alpha_1$ $1.081\alpha_2$	1 1
631	1.054	1.051	1	1.054	1.047	1
444	1.032	[2]	15	1.031	$1.035\alpha_1$ $1.034\alpha_2$	1 1

[1] These two lines may belong to the tetragonal phase.

[2] A very diffuse line that could not be measured.

Note: Only those lines which index in terms of a taenite supercell are listed in this table. Other lines present on the films index in terms of a kamacite supercell (Table 4). A number of large discrepancies between d_{obs} and d_{calc} are the result of errors made when measuring the position of the lines (see *note*, Table 2).

supercell with $A=3a$ (Tables 3, 4). Nine very faint lines on this film cannot be measured. The unit cell edge of the taenite supercell is approximately 7.146 Å. The drilled sample yields a pattern containing only nine lines (Table 5), five belonging to a face-centered cubic taenite with cell edge (a) approximately 3.589 Å, and four belonging to a body-centered

TABLE 4. d-VALUES OF THE KAMACITE

hkl	Twin City (D)		Linville (D)			Carlton (Of)			Mesa Verde Park (Om)		
	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}
200	—	—	4.301	4.495	1	4.308	4.399	30	—	—	—
220	—	—	3.043	3.032	10	—	—	—	—	—	—
221	—	—	2.868	2.953	10	—	—	—	—	—	—
320	—	—	2.386	2.455	5	—	—	—	—	—	—
321	—	—	2.299	2.227	1	—	—	—	—	—	—
400	—	—	2.151	2.124	1	2.154	2.124	1	—	—	—
322	—	—	2.086	2.097	1	2.090	2.101	10	—	—	—
330/411	2.026	100	2.028	2.031	100	2.031	2.031	100	2.029	2.031	100
331	—	—	1.973	1.967	60	—	—	—	—	—	—
332	—	—	1.925	1.824	5	1.927	1.828	5	—	—	—
430	—	—	1.721	1.699	1	—	—	—	—	—	—
530/333	1.490	1	1.656	1.481	10	1.659	1.490	10	1.657	1.490	30
600/442	1.433	10	1.434	1.435	30	1.436	1.435	50	1.435	1.435	40
542	—	—	1.242	1.278	1	—	—	—	—	—	—
640	—	—	1.193	1.197	1	—	—	—	—	—	—
721	1.169	50	1.170	1.170	70	1.173	1.171	70	1.171	1.171	70
642	—	—	1.150	1.153	1	—	—	—	—	—	—
				$1.015\alpha_1$	10						
822/660	—	—	1.014			—	—	—	1.015	1.015	40
				$1.015\alpha_2$	10						

Note: Only those lines which index in terms of a kamacite supercell are listed in this table.

cubic kamacite with unit cell edge approximately 2.869 Å. As with the Twin City the unit cell edge of the taenite in the drilled sample is half that of the taenite in the scratch sample.

Examination of the other powder patterns has shown the presence of the taenite supercell in the medium octahedrite Mesa Verde Park. However, the x-ray pattern of this meteorite is predominantly due to kamacite and the tetragonal phase and, as a result, the taenite lines are only faintly visible. Only three of the measurable lines belong to the taenite supercell but other very faint lines on the film can be recognized as belonging to this pattern even though they cannot be measured. An x-ray film of the drilled sample of this meteorite contains only the simple kamacite and taenite patterns with the kamacite predominant (Table 5).

Composition of the taenite. A curve relating the composition of γ Fe-Ni alloys to the unit cell edge has been established by Jette and Foote (1936), Bradley *et al.* (1937) and Owen and Yates (1937). We have analyzed a series of synthetic γ alloys and, except at 80% nickel, our data fall on this curve (Fig. 1).

According to this curve, the taenite drilled from the Twin City meteorite averages about 28% nickel. This value is in reasonable agreement with the reported bulk nickel content of the meteorite (29.91%—Mason

TABLE 4—(*continued*)

Linwood (Ogg)			Bischtübe (Og)			Union (H)			Hex River Mountain (H)		
d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}	d_{calc}	d_{obs}	I_{rel}
—	—	—	4.304	4.340	30	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
2.873	2.844	10	—	—	—	—	—	—	2.876	2.883	1
—	—	—	2.388	2.477	1	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	2.087	2.088	1	—	—	—	—	—	—
2.032	2.031	100	2.029	2.031	100	2.022	2.031	100	2.033	2.031	100
1.977	1.914	5	—	—	—	1.968	1.993	10	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
1.724	1.714	1	—	—	—	—	—	—	1.725	1.724	1
—	—	—	1.657	1.490	10	1.651	1.486	60	—	—	—
1.437	1.435	70	1.435	1.433	60	1.430	1.431	1	1.438	1.422	70
—	—	—	—	—	—	1.239	1.286	1	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
1.173	1.171	100	1.171	1.171	80	1.168	1.170	20	1.169	1.171	80
—	—	—	—	—	—	—	—	—	—	—	—
1.016	1.016	80	1.015	1.014	65	—	—	—	1.016	1.014	70

1962), and with a modal analysis which indicates that the meteorite contains 93.2 vol% taenite. Similarly, the *x*-ray data for the Linville meteorite indicate that the taenite in the drilled sample contains about 32% nickel. It must of course be recognised that taenite in meteorites is of extremely variable composition, (Feller-Kniepmeier and Uhlig 1961; Goldstein and Ogilvie, 1965), and that the nickel content can exceed 50% in those regions close to a taenite/kamacite interface. Hence, compositions determined by *x*-ray means are, at best, only average values for the taenites contained in the samples.

Possible framework for the taenite superlattice. A possible framework for the taenite superlattice is illustrated in Fig. 2. This structure is formed by combination of eight body-centered cubic cells. Nickel atoms occupy four of the body-centered sites in such a way as to avoid being nearest neighbours and to avoid being in cubes that are side by side. With the four nickel sites fully occupied as shown, the structure corresponds to the composition Fe_3Ni. Hume-Rothery and Raynor (1962) have pointed out that:

"Since the compositions A_3B and AB usually mark definite states in the completion of zones of solute atoms, we may always expect superlattice formation at those compositions at low temperatures if the size factors are suitable."

TABLE 5. d-VALUES OF THE DRILLED SAMPLES

hkl	Union (H)		Hex River Mountain (H)		Horse Creek (H)		Linwood (Ogg)		Bischtübe (Og)		Mesa Verde Park (Om)		Carlton (Of)		Linville (D)		Twin City (D)	
	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}
	2.234[1]	1	2.224[1]	1	2.233[1]	1	—	—	2.225[1]	1	2.235[1]	5	2.237[1]	1	2.232[1]	1	2.272[1]	5
	—	—	—	—	—	—	—	—	—	—	2.179[2]	1	—	—	—	—	—	—
111γ	—	—	—	—	—	—	—	—	—	—	2.070	10	2.070	50	2.065	80	2.067	100
110α	2.024	100	2.024	100	2.021	100	2.019	100	2.020	100	2.025	100	2.026	100	2.014	100	2.022	70
200γ	—	—	—	—	—	—	—	—	—	—	too faint		1.794	10	1.794	40	1.788	80
	1.713[1]	1	—	—	—	—	—	—	—	—	—	—	—	—	1.711[1]	1	—	—
200α	1.431	60	1.435	60	1.429	50	1.431	50	1.431	60	1.435	50	1.433	60	1.435	50	too faint	
220γ	—	—	—	—	—	—	—	—	—	—	—	—	1.269	10	1.268	40	1.266	70
211α	1.170	80	1.170	80	1.168	80	1.171	80	1.173	80	1.171	80	1.171	80	1.171	80	1.167	30
311γ	—	—	—	—	—	—	—	—	—	—	—	—	1.084	5	1.082	50	1.080	80
222γ	—	—	—	—	—	—	—	—	—	—	—	—	too faint		1.035	30	1.034	70
220α	1.014	70	1.014	70	1.013	60	1.014	70	1.014	70	1.014	60	1.015	70	1.014	60	too faint	
	a		*a*		*a*		*a*		*a*		*a*		*a*		*a*		*a*	
	2.867_8 Å		2.868_2 Å		2.864_1 Å		2.870_0 Å		2.868_7 Å		2.868_8 Å		2.870_1 Å		2.869_6 Å		—?—	
	—		—		—		—		—		—?—		3.595 Å		3.589 Å		3.582 Å	

[1] Tungsten carbide impurity.
[2] (400) reflection of kamacite supercell.

Bradley and Jay (1932) originally proposed the above structure for ordered iron-aluminum alloys. They showed that aluminum entered the body-centered sites (occupied by nickel in Fig. 2) until the composition Fe_3Al was reached. On further addition of aluminum, the aluminum atoms distributed themselves on all eight body-centered sites until, at the composition FeAl, these were all occupied by aluminum, giving a caesium chloride structure, It is suggested that the nickel atoms in taenite may

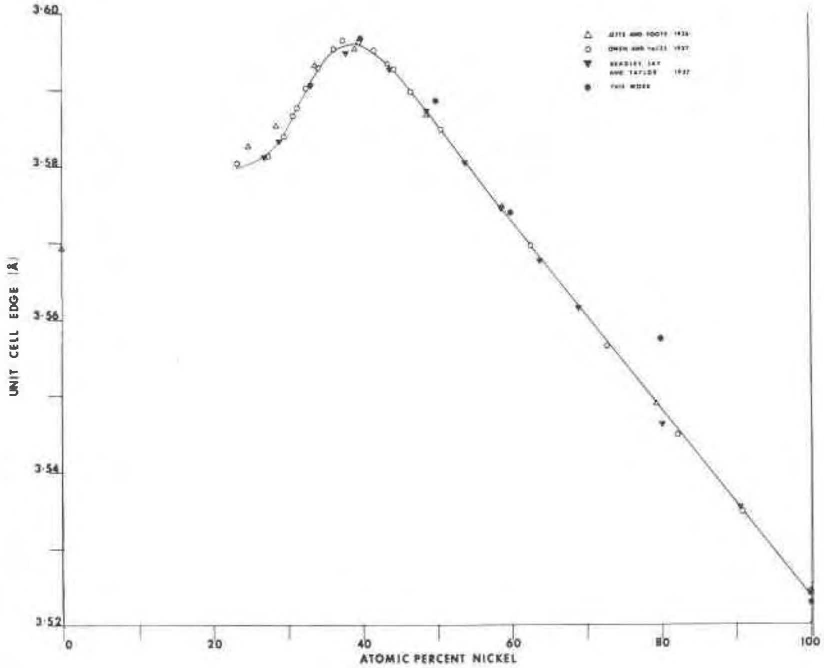

FIG. 1. Relationship between unit cell edge and composition in γ Fe-Ni alloys.

behave in an analogous manner and exhibit superlattice formation over a range of composition in the region Fe_3Ni.

Unfortunately, the calculated structure amplitudes for the proposed structure show that this model would not give rise to the large number of superlattice reflections observed in the taenite and hence the model is not a complete explanation of the patterns. Nevertheless, the general agreement between the taenite compositions and the composition of the model would suggest that the concept is basically correct. Possibly small displacements of the atoms within the structure might give rise to a model able to satisfy the complex conditions required to obtain the observed superlattice reflections. We are unable to propose a detailed structure for such a model but would note that magnetic exchange forces within the lattice might cause the necessary displacement of the atoms.

Ordering has not been detected in Fe_3Ni in the laboratory, although Hoselitz (1944) suggested that it might occur. However, on the basis of electrical and magnetic measurements, order has been reported at the composition $FeNi_3$ (Wakelin and Yates 1953) and at the composition FeNi (Paulevé, *et al*, 1962). In view of the great age of meteoritic iron

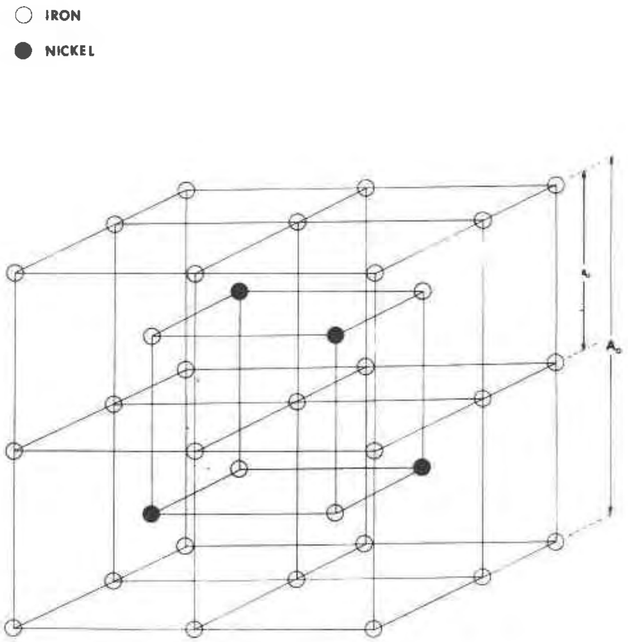

FIG. 2. Possible framework for the taenite superlattice.

it would seem reasonable to conclude that the superlattice formation is primarily an ordering phenomenon.

THE KAMACITE SUPERSTRUCTURE

Evidence for a kamacite superstructure. The evidence for a kamacite superstructure appears only in the x-ray powder patterns of scratch samples; it is absent from the corresponding drilled samples. The evidence is well documented in all of the patterns (Table 4) except that of the Horse Creek meteorite, and it is particularly evident in the Linville and Carlton meteorites.

As mentioned earlier, the x-ray pattern of the Linville meteorite contains 46 measurable lines. Of these, 27 belong to the taenite superstructure (Table 3). The remaining 19 lines can be indexed on the basis of a cubic unit cell (Table 4) in which the cell edge is approximately 8.603 Å. Nine very faint lines on the film cannot be measured. The drilled sample yields a pattern containing only nine lines (Table 5), five of which belong to a face-centered cubic taenite in which the cell (a) is approximately 3.589 Å, and four of which belong to a body-centered cubic kamacite in which the unit cell edge (a) is approximately 2.869 Å. It is clear that the unit cell edge of the kamacite in the drilled sample (disordered) is one third that of the kamacite in the scratched sample. This relationship also holds for the other meteorites that have been examined:

	Scratch Sample (Å)	Drilled Sample (Å)
Union	8.58	2.868
Linwood	8.620	2.870
Bischtübe	8.608	2.869
Mesa Verde Park	8.609	2.869
Carlton	8.617	2.870

Composition of the kamacite. The composition of the kamacite in these meteorites is not known accurately at this time but it may be estimated from the unit cell edge of the drilled kamacite. We have measured the unit cell edge of zone refined iron and of 2%Ni and 4%Ni synthetic alloys at 25° C., and have used the data to set up a composition/cell edge curve. Unfortunately, an allegedly 6%Ni alloy was found to contain both α and γ phases and could not be used in this work. However, according to the electron probe measurements of Feller-Kniepmeier and Uhlig (1961), kamacite in the Grant meteorite contains 6.6% nickel, and kamacite drilled from this meteorite in the present work has a unit cell edge of 2.869_5 Å. This information has been combined with the data of the synthetic alloys to obtain a composition/cell edge curve that is applicable to the present work (Fig. 3).

Jette and Foote (1936) have also measured the unit cell edges of synthetic α Fe-Ni alloys at 25° C. Their original data have been converted from kX to Å by multiplying by 1.00202 and the results are shown in Fig. 3. The differences between the two curves probably represent experimental errors on our part. The samples used in the present work have not been annealed and hence the x-ray films contain broad lines due to distortion of the metal. These lines do not separate into $\alpha_1\alpha_2$ doublets at high 2θ, and errors probably arise when measuring their positions. However, such errors also appear in the data for the drilled kamacites and therefore do not affect the results when using our own curve.

All the drilled samples have been x-rayed at 25° C. The results indicate kamacite compositions ranging from 3.5%Ni to about 7.8%Ni. In particular, the x-ray data indicate that kamacite in the Linville meteorite contains about 6.6%Ni and kamacite in the Carlton meteorite contains

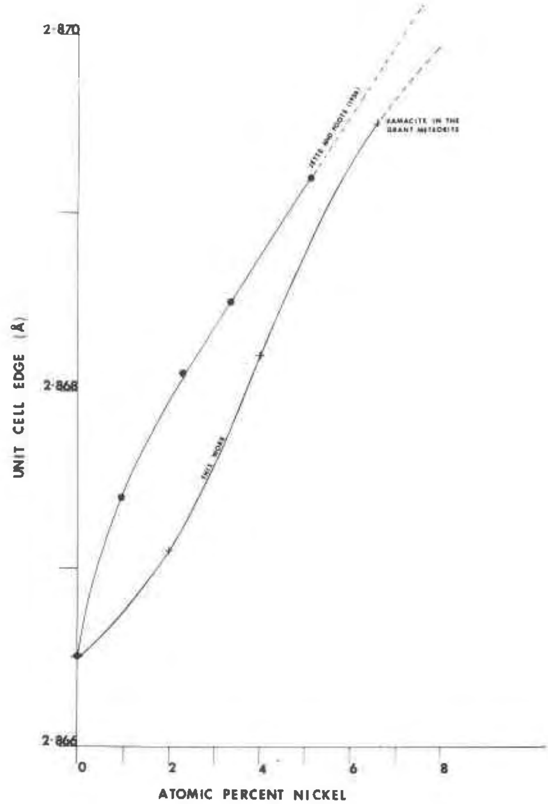

Fig. 3. Relationship between unit cell edge and composition in α Fe-Ni alloys.

about 7.8%Ni. As with taenite it must be recognised that the x-ray method indicates only the average nickel content of a sample.

Possible framework for the kamacite superlattice. By analogy with the previously described taenite supercell, a possible framework for the kamacite supercell is shown in Fig. 4. The supercell is formed by combination of 27 body-centered cubes with nickel atoms occupying four of the body-center sites. The nickel atoms are distributed in such a way as to avoid being nearest neighbours and to avoid being in adjacent cubes. With the four nickel sites fully occupied, as shown, this model has the composition of 7.8% nickel. It is significant that this is essentially the same composition as that indicated for the kamacite in the Carlton meteorite, and is close to the composition indicated for the kamacite in the Linville meteorite. The kamacite supercell reflections are particularly well developed in both these meteorites. Furthermore, no kamacites are known to contain more than 7.8% nickel.

As with the taenite supercell, it is necessary to postulate a more complex model in order to account for the many observed supercell reflections, and it is suggested that magnetic exchange forces within the lattice

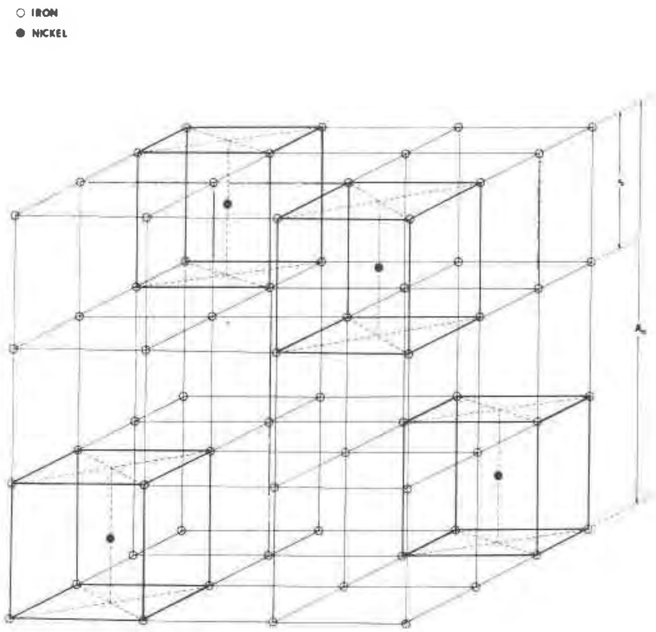

FIG. 4. Possible framework for the kamacite superlattice.

might cause small displacements of the atoms in such a way that the necessary conditions for diffraction are satisfied.

SIGNIFICANCE OF THE KAMACITE AND TAENITE SUPERSTRUCTURES

Wakelin and Yates (1953) have demonstrated the existence of ordering in the region $FeNi_3$ by measuring the electrical resistivity and magnetic properties of synthetic iron-nickel alloys. They found that ordering was extremely sluggish and took place over a range of composition from 50 to 80 atomic per cent nickel, with the maximum change in structure sensitive properties occurring at the composition $FeNi_3$. More recently, Paulevé *et al.* (1962) have demonstrated the existence of a CuAu type superlattice in a synthetic alloy of composition FeNi (50:50). However, ordering was so sluggish that it could only be established under neutron irradiation in a magnetic field. Since taenite and kamacite contain far less nickel than these synthetic alloys it follows that ordering, if it occurs, should be an extremely sluggish process. However, in view of the great age of meteoritic iron, (about 4×10^9 years), it would seem reasonable to conclude that superlattice formation is indeed an ordering phenomenon.

Since the critical temperature for ordering of iron-nickel alloys are low, (498° C. for FeNi3—Wakelin and Yates 1953, 320° C. for FeNi—Paulevé *et al.* 1962), it is probable that the critical temperatures for ordering of taenite and kamacite are equally as low, if not lower. It follows, therefore, that if ordering has taken place, then the meteorites must have cooled to these temperatures at some time in the past sufficiently remote to allow formation of the superstructures to take place. If the critical temperatures were known and details of the superstructures could be determined then, in principle, it should be possible to calculate the time required for formation of the superstructures and hence obtain a better insight into the cooling histories of these bodies.

The Anomalous Horse Creek Meteorite

The Horse Creek meteorite is a hexahedrite (Table 1). However, it has long been known as an anomalous iron because of its unusual pseudo-octahedral structure. The pesudo-octahedral structure arises through orientation of schreibersite and perryite lamellae along what appear to be octahedral planes in the metal, thus producing a prominent Widmanstätten pattern. However, Perry (1944) has pointed out that these planes are not really octahedral and that sections of the meteorite in which they intersect at right angles show a rectangular pattern not a square one.

The *x*-ray pattern of the scratch sample is unusual among all the meteorites examined in that it does not contain kamacite lines. However, it does contain a well developed tetragonal pattern (Table 3). The cell dimensions of this phase are approximately $a=7.16$ Å and $c=5.81$ Å. As with the other meteorites, the tetragonal phase is unstable and converts to a cubic "kamacite" in the drilled powder. However, the unit cell edge of this "kamacite" is anomalously small (Table 5) and is in fact far smaller than that of pure α-iron.

Besides the materials here discussed, we have *x*-rayed an additional 16 iron meteorites as drilled powders. All show the simple patterns of kamacite and/or taenite. Moreover, out of the total of 25 meteorites only the "kamacite" in the Horse Creek meteorite has given this unusually low value for the unit cell edge.

Using an electron probe microanalyzer, Fredricksson and Henderson (1965) have shown that the "kamacite" contains 2.5% silicon in solid solution together with about 3.9% nickel and that the meteorite also contains about 3% of perryite, nickel silicide, a new mineral having the approximate composition Ni 81%, Si 12%, Fe 3% and P 5%. It seems, therefore, that the Horse Creek meteorite is indeed an anomalous iron. Apparently the presence of silicon markedly reduces the cell edge of kamacite, and silicon may also be responsible for the greater stability of the tetragonal phase in this meteorite. This stability is indicated by the lack of kamacite in the scratch sample and the apparently tetragonal orientation of the schreibersite lamellae.

Conclusions

The metallic phases in iron meteorites have been invesitgated by *x*-ray analysis. It has been found that

(1) many iron meteorites contain a metastable tetragonal phase that seemingly has the same composition as kamacite and is indistinguishable from this mineral under the microscope, (2) kamacite and taenite in iron meteorites have superstructures and (3) both the tetragonal phase and the kamacite and taenite superstructures are destroyed when material is drilled from the meteorites.

It has been concluded that the tetragonal phase is a transitional stage in the transformation of γ-phase into α-phase (kamacite).

Because synthetic iron-nickel alloys are known to order on the laboratory time scale it has been concluded that the kamacite and taenite superstructures are due to an ordering process. However because of the small difference in scattering powers between Fe and Ni, simple ordered structures would not produce visible *x*-ray superstructure reflections. In order to produce the large number of observed superstructure reflections a more complex model must be postulated in which the ordered atoms are systematically displaced in position, possibly as a result of magnetic exchange forces. A detailed structure determination by neutron diffraction would be needed to verify such a model.

The *x*-ray data for the Horse Creek meteorite indicate that it has an unusual composition. Recent work by Fredricksson and Henderson (1965) has shown that silicon is present in the metallic phase of this meteorite.

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