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MELLON INSTITUTE

SEMI-ANNUAL REPORT

on

X-RAY DETECTION OF DISORDERED ORTHOPYROXENES IN METEORITES

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by

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Introduction

Since June 1, pyroxenes from approximately 60 meteorites have been examined by means of the Debye-Scherrer powder technique. Crystals from about one third of these have also been examined using oscillation and Weissenberg single-crystal techniques.

The powder technique is most useful when patterns of a rather pure pyroxene can be used. In some samples the kamacite, taenite, sulfides and olivine were removed by boiling in 6N hydrochloric acid. Usually 0.1-0.2 g samples were ground to less than 0.5 mm diameter and boiled from 1 to 5 minutes, depending on the amount of metal present, in 30 ml of acid. This treatment usually left a sample consisting of pyroxene alone or mixed with plagioclase. In some cases, small amounts of other minerals such as quartz, tridymite or cristobalite also appeared in the residue. The presence of small amounts of plagioclase can make the identification of disordered orthopyroxene in a mixture with clinoenstatite, pigeonite or orthopyroxene very difficult or impossible. This difficulty arises because the pyroxenes themselves have fairly similar patterns and the strongest line of plagioclase feldspars is about 3.20A, the same as the strongest line of enstatite. Table I lists the *d* spacings and intensities for Bamle enstatite, clinoenstatite, bytownite, and Cumberland Falls achondrite, which contains a large amount of disordered enstatite and a small amount of clinoenstatite.

Since the pyroxenes and plagioclase in meso-siderites can usually be separated quite easily and the amount of plagioclase in the enstatite chondrites is small, the powder technique has been more help with these two groups than with those which contain larger amounts of plagioclase.

Single-crystal Photographs

The powder x-ray technique can usually be successful in identifying minerals. However, when several closely related minerals are possibly present in a sample, then the single-crystal technique can be used to detect differences than can't be noticed in the powder technique. From a series of Weissenberg, or other single-crystal photographs, the intensity and shape of all possible ($hk\ell$) reflections can be examined. The Weissenberg camera has been used in this work because it has a short sample to film distance, approximately 29 mm. Since most of the crystals are very small, (approximately 0.10 x .05 x .05 mm) the exposure time of techniques using larger sample to film distances would be much longer. Copper radiation was used in most of this work and all the figures shown were obtained with this radiation.

When a pyroxene crystal is oriented with its $\underline{c}$ axis parallel to the long axis of a cylindrical camera and allowed to oscillate approximately 20° a pattern such as seen in Figure 1 is obtained and is called an oscillation photograph. From this type of photograph, the repeat distance along the $\underline{c}$ axis can be calculated. The parallel rows of spots are called layer lines, the central one is the 0 layer, and the lines above the 0 layer are numbered 1 and 2 and the ones below are $\bar{1}$ and $\bar{2}$. A Weissenberg photograph permits the recording of all the spots on one layer line to be spread over the whole film. Figure 2 contains the *hkl* and $hk\bar{l}$ net from an ordered orthorhombic enstatite from New Guinea, oscillated about the *c* axis. Figure 3 shows the *hkl* Weissenberg pattern of an untwinned clinopyroxene.

Figure 4a shows a template used to show parallel lattice row lines for the kind of Weissenberg photographs we have used. In Figure 4b the template is aligned to show reciprocal lattice rows, or festoons, parallel to the *a** direction of an *hkl* net of Kota-Kota. The prominent festoons which show up clearly without a template are parallel to the *b** direction.

The Weissenberg and oscillation photographs give a picture of the reciprocal lattice rather than the direct lattice so that along any axis the festoons, or lattice rows of spots, are closer together for a larger dimension than for a smaller one. Therefore, the festoons parallel to the *a** direction of enstatite (*a* = 18.2) are closer than the festoons parallel to the *a** of the clinopyroxene of Figure 2 (*a* = 9.1).

A Weissenberg (*hkl*) photograph from enstatite crystals should show symmetry about the *a** and *b** axes, while *hkl* photographs of clino-enstatite should only show symmetry about the *a** axis. On a photograph from enstatite spots *hkl* and $h\bar{k}l$, and *hkl* and $\bar{h}kl$ have identical intensities and positions. For an untwinned clinopyroxene, only spots *hkl* and $\bar{h}kl$ have this relationship. Twinned clinoenstatite, Figure 6 appears to have a smaller *a** (larger *a* axis) than enstatite or untwinned clinopyroxene and orthorhombic symmetry. The apparent *a** (it should be the same as in Figure 2), and the false symmetry are caused by the twinning. Figure 7, a pattern from the Pesyanoe achondrite, is an ideal type of disordered orthorhombic enstatite. All enstatite hkl reflections are present on the film, but spots with h even are more diffuse and elongated parallel to a*. Figure 8 from the Norton County achondrite is similar to Figure 7 except that it contains some additional spots due to the presence of twinned clinoenstatite. All disordered crystals from the enstatite achondrites (Brown and Smith, Pollack and Ruble, Pollack) gave patterns very similar to these two figures except that in some cases the crystals were more highly shattered.

In addition to these types of patterns, Brown and Smith (1963) have observed patterns that varied considerably between the two extremes of twinned clinoenstatite and enstatite on synthetic and meteoritic enstatites heated up to 1230°C. They grouped all disordered structures into two groups, D-clino, for those which resembled twinned clinoenstatite and D-ortho for those closer to orthohombic enstatite. The structural differences between the $MgSiO_3$ polymorphs is discussed in detail by Brown, Morimoto, and Smith (1961). Disordered enstatites and clinoenstatites form when stacking faults parallel to a* of these minerals are closely spaced and irregularly arranged, (Brown and Smith, 1963).

Enstatite Chondrites

Mason in his description of the chemical composition and mineralogy of enstatite chondrites found that nine contained mainly orthorhombic enstatite and six were predominantly clinoenstatite. In our study of the pyroxenes in these meteorites using single-crystal techniques, we have found differences within the enstatite and clinoenstatite groups, which are not easily measured using optical or powder diffraction techniques. Samples from all of the enstatite chondrites were first examined using the Debye-Scherrer technique and the results are listed in Table II. Eight gave patterns of well crystallized enstatite. One pattern of St. Mark's indicated it was well crystallized and a second one that possibly some disordered enstatite was present. The patterns from Bethune and Adhi Kot were identified as clinoenstatite and others appeared to be mixtures of enstatite, clinoenstatite and disordered enstatite. Single-crystal oscillation and (hkl) Weissenberg photographs were then prepared of crystals from all the enstatite chondrites except Adhi Kot and Bethune. No crystals suitable for single-crystal x-ray work could be found in our samples of these two meteorites. That is, no crystals at least 0.1 mm long were found when the samples were examined under the microscope.

The Weissenberg patterns from one crystal of each well crystallized enstatite were examined and none showed evidence of disorder or the presence of clinoenstatite.

The disordered patterns produced by the Abee, St. Mark's, St. Sauveur, Indarch and Kota-Kota are all different from those produced by achondritic disordered enstatites. Patterns from the last group all contain some diffuse and some sharp spots while those from St. Mark's, St. Sauveur, and Abee only contained extra streaks between the normal enstatite spots. These streaks are along festoons parallel to a^*. Most of the patterns also showed a few spots which are probably due to the presence of twinned clinoenstatite or possibly other clinopyroxene.

None of the crystals were perfect and all showed some splitting of the spots. Two crystals from Kota-Kota, Figure 4b, and three from Indarch (isolated from chondules) were also examined. These crystals were also split, but the patterns they produced showed them to be mainly twinned clinoenstatite. They contained streaks similar to the Abee, St. Mark's and St. Sauveur (Figure 5) crystals as well as diffuse spots due to disordered enstatite. Crystals from Indarch are more highly shattered than the Kota-Kota crystals and each spot on Indarch patterns is elongated along a line of constant 2θ. The Indarch and Kota-Kota contained the same sharp and diffuse spots of the achondrites, but the sharp clinoenstatite spots are much stronger and the diffuse disordered enstatite spots much weaker.

The single-crystal patterns further delineate differences between the pyroxenes in the enstatite chondrites. If the enstatite chondrites are considered a series with enstatite on one end and clinoenstatite on the other, the x-ray data is useful in distinguishing between members of the series although it does not tell why the differences occur. If more information were known about the effect of various quench conditions on clinoenstatite, the x-ray single-crystal data might be more useful in interpreting the various Weissenberg patterns obtained from St. Mark's, St. Sauveur, Abee, Kota-Kota and Indarch. Since these results, as well as the results from other meteorites discussed later are based on the examination of approximately 1 gram of each sample or less, the study of larger samples might show more variability than we have found. If the type of clinoenstatite found in Kota-Kota and Indarch is related to their chondrules, then clinoenstatite might reasonably be expected in two other enstatite chondrites, Huittinen (Hvittis) and Daniel's Kuil, in which Mason (1966) found barely recognizable chondrules.

The single-crystal results are different from the powder data for the St. Mark's, St. Sauveur, Abee and Kota-Kota. This result might be expected if the few more perfect crystals were different structurally from the fine grained material which makes up the larger portion of the samples. Examination of a larger number of single-crystals might give results more similar to the powder work.

Meso-siderites

The pyroxenes from eight meso-siderites have been studied by the powder method and one by single-crystal techniques. In six meso-siderites (Bondoc, Clover Springs, Estherville, Hainholz, Mt. Padbury, and Patwar) the pyroxene was found to be ordered orthopyroxene. Weatherford contains clinoenstatite and Crab Orchard contains pigeonite. Single-crystal patterns of the Weatherford show that the crystals are highly shattered twinned clinoenstatite.

Other Chondrites

The powder results from all the other chondrites we have studied are grouped together in Table III. Most of the meteorites listed in the table are the olivine bronzite and olivine hypersthene chondrites of Mason (1962), and includes both the "ordinary" and "unequilibrated" chondrites of Van Schmus and Wood (1966).

Almost all the samples from this group of meteorites were acid treated to simplify the separation of the pyroxene. Suitable samples from Ochansk, Chainpur and Bjurbole were obtained without acid treatment because their well defined chondrules were easily isolated from the meteorite fragments. Of 39 ordinary chondrites, the powder technique indicated that disordered orthopyroxene was present or probably present in seven. Using single-crystal techniques, it has been found in three of the seven. In three others, no single crystal work has been carried out as yet. Bremervörde is the only one so far where we have looked for disordered crystals based on powder work and not found them. Although the powder photographs of Chainpur did not indicate the presence of disordered crystals, a number of single-crystals were mounted and examined. Five crystals of twinned clinoenstatite were found before a disordered crystal was selected and we, therefore, feel that with additional work disordered crystals will be located in Bremervörde.

In the present work, disordered orthopyroxene crystals have been found in Soko Banja* and Ochansk. The crystal from Ochansk* was similar to Norton County in that it consisted partially of twinned clinopyroxene. Crystals similar to those from Kota-Kota were found in Chainpur, Clovis and Hamlet, Figure 9. In these crystals, the intensity of the twinned clinoenstatite spots is greater than the intensity from the disordered enstatite. The disordered crystals from these four chondrites

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*Keil and Fredrickson, 1964 found 22.7 and 15.6 Mole % iron in orthorhombic pyroxenes from Soko Banja and Ochansk.

appear to be similar to some of the disordered clinoenstatite found by Brown and Smith (1963) after crystals were heated above 1000°C and quenched to 20°C.

Table IV list the number of single crystals from chondrites other than enstatite chondrites, which have been examined, and their composition. All the twinned clinoenstatite crystals from chondrites that have been examined to date have shown some streaking parallel to the $\underline{a}^*$ axis. Crystals of enstatite from Bamle, Norway, heated to produce clinoenstatite show similar streaks. Two crystals of twinned clinoenstatite from New Guinea have also been examined. One crystal had very weak streaks but, in addition, had weak orthoenstatite spots. The other crystal was split but did not appear to have streaks. The chondrites in which disordered orthopyroxenes have been found are in the petrologic types 3 and 4 of Van Schmus and Wood (1966). Petrologic type 3 or groups H3, L3, and LL3 contain the "unequilibrated ordinary chondrites" of Dodd and Van Schmus (1965). In previous work, (Pollack, 1966) disordered orthopyroxene crystals were also found in the Hugoton, which is in group H5. Too few chondrites have been adequately studied to determine whether or not disordered pyroxene is really more common in the unequilibrated chondrites than in the more recrystallized ones. Brown and Smith (1963) reported the synthesis of disordered enstatite by quenching from 1450°C and some of the disordered crystals from the chondrites may have also formed by quenching. It still has not been determined whether or not disordered orthopyroxene can result from shock effects but the inversion of strained enstatite, under 5000 bars pressure at 500-800°C (Turner, Heard and Griggs, 1960) to clinoenstatite suggests that it is a very likely possibility.

Summary and Discussion

Both powder and single-crystal diffraction techniques have been used in the detection of disordered orthopyroxene in the meso-siderites, enstatite chondrites, and "ordinary chondrites." The powder technique has been most useful in identifying the pyroxene in the first two groups because they are more uniform and contain less plagioclase than the "ordinary chondrites." Ordered orthopyroxene has been identified as the only pyroxene in six meso-siderites and clinoenstatite and pigeonite were each found in one other. In the enstatite chondrites, the ordered orthorhombic enstatite is the major constituent of eight, clinoenstatite the major constituent of two, and the others are mixtures of enstatite disordered enstatite and clinoenstatite.

The disordered enstatite crystals in the enstatite chondrites show much greater variation than those found in the enstatite achondrites. All the disordered enstatites from the achondrites were either similar to the (hkl) Weissenberg pattern of the Norton County shown in Figure 8 or were highly shattered crystals in which the spots due to twinned clinoenstatite could not be seen. No crystal from the enstatite chondrites gave a pattern similar to the Norton County.

Disordered orthopyroxene was found in five crystals from the "ordinary" and "unequilibrated" chondrites. One contained no clinopyroxene, one contained a small amount of clinopyroxene and three contained more clinoenstatite than disordered enstatite.

Brown and Smith (1963) mentioned that $MgSiO_3$ crystals quenched from 1450°C gave a wide variety of single-crystal patterns, some similar to twinned clinoenstatite and others were disordered enstatite and disordered clinoenstatite. Of all the enstatite chondrites Adhi Kot, Bethune, Indarch, and Kota-Kota are the ones that would be most likely to have quenched pyroxene. The first two did not have suitable single-crystals while in the latter two the crystals from each meteorite were very similar. However, additional crystals need to be examined before the uniformity within each of these can be truly assessed. Nonuniform clino-pyroxenes structure as indicated by single-crystal patterns may provide a way of distinguishing quenched pyroxenes in chondrites.

Disordered orthopyroxenes have been detected in five enstatite and five other chondrites and shows that the structural state of the pyroxenes in these chondrites is more varied than had been realized. Since the disordered crystals from Chainpur and Ochansk had been isolated from well-formed chondrules, it is likely that these crystals developed as the chondrule was formed, probably as a result of quenching. The other crystals may have formed in a similar way or as a result of shock deformation or metamorphism.

Sidney S. Pollack:mas

FELLOW
X-RAY DIFFRACTION

R: 12-6-1966
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Table I

Power Data for Bamle (Ordered Enstatite), Clinoenstatite, Cumberland Falls Achondrite, Bytownite, 77.0% An.

Bamle Enstatite[1]		Clinoenstatite[2]		Cumberland Falls[1]		Low Bytownite[3]	
d(Å)	Intensity	d(Å)	Intensity	d(Å)	Intensity	d(Å)	Intensity
6.33	21	6.36	4	6.3	W	6.52	4
4.43	3	4.413	12	4.41	8	4.69	5
4.028	1					4.032	8
3.314	6	3.287	48	3.30	15	3.888	5
U 3.233	1					3.748	8
3.175	100	3.174	56	3.17	84	3.624	7
U 3.122	2					3.459	5
U 3.049	5	2.98	96	2.96	28	3.411	4
2.946	16	2.887	4	2.94		3.357	6
2.878	54	2.878	100	2.87	100	3.257?	5
2.832	9	2.803	8	2.82	W	3.229	5
						3.196	10
						3.165	8
						3.122	6
						3.017	5
						2.945	7
						2.922	5

U = Unidentified line

W = Weak diffuse line

1. S. S. Pollack and W. D. Ruble, Am. Min. **49**, 983, 1964.
2. H. Kuno and H. H. Hess, Am. J. Sci. **281**, 741, 1953.
3. J. Goodyear and W. J. Duffin, Miner May **30**, 306, 1954.

Table II

Type of Pyroxene Indicated by Debye-Scherrer

Patterns of Acid Treated Enstatite Chondrites

Meteorite	No. of Patterns	Type of Pyroxene	Van Schmus & Wood Group 1966
Atlanta	3	Enstatite	E5
Blithfield	2	"	E6
Daniel's Kuil	1	"	E6
Huittinen (Hvittis)*	2	"	E6
Khairpur	2	"	E6
Jajh de Kot Lalu	2	"	E6
Pillistfer	1	"	E6
Ufana	1	"	E6
Bethune	1	Clinoenstatite	
Adhi Kot	1	"	E3
St. Mark's	1	Enstatite	E5
	1	Enstatite & disordered enstatite	
Abee	3	Disordered enstatite (major) Clinoenstatite (minor)	E4
St. Sauveur	2	Clinoenstatite enstatite	E4
Indarch	2	Clinoenstatite (major) disordered enstatite (minor)	E4
Kota-Kota	3	Disordered enstatite (major) clinoenstatite (minor)	E4

*O. Näykki of the Kivimuseo, Helsinki, informed me that the correct name of the locality is Huittinen, not Hvittis as it is usually listed in catalogues.

Table III

Type of Pyroxene Identified in Chondrites

by Means of Debye-Scherrer Patterns

Meteorite	Pyroxene Identified	Van Schmus & Wood Group (1966)
Akron	Ortho	Not Given
Appley Bridge	Ortho	LL6
Arriba	Ortho	L5
Barrata	Clino; Possibly Ortho	L3
Beenham	Ortho	L5
Bremervörde	Ortho and Disordered Ortho	H3
Bjurbole	Ortho and Clino	L4
Calliham	Ortho	Not Given
Cashion	Ortho	"
Chainpur	Clino	LL3
Chandakapur	Clino	L5
Chateau Renard	Clino	L6
Clovis	Clino and Ortho or Disordered Ortho	H3 or H6
Coolidge	Clino; Possibly Ortho	C4
Cullison	Clino; Possibly Ortho	H4
Cynthiana	Clino; Possibly Ortho	L4
Dimmitt	Clino; Possibly Ortho	H(3,4)
Drake Creek	Ortho	L6
Gnadenfrei	Ortho; Probably Disordered Ortho	H5
Hallingeberg	Ortho and Clino	H3

Con't.

Table III - Con't.

Hamlet	Clino; Possibly Ortho	LL3,4
Holbrook	Ortho	L6
Lua	Clino; Possibly Ortho	L5
Mangwendi	Ortho	LL6
Ochansk	Ortho; Disordered Ortho	H4
Ottawa	Ortho	LL6
Pantar	Ortho	H5
Parnallee	Clino; Ortho or Disordered Ortho	LL3
Plainview	Ortho	H5
Potter	Ortho	L6
Prairie Dog Creek	Clino; Possibly Ortho	H3
Richardton	Ortho	H5
Roy	Ortho	L6
St. Mesmin	Ortho	LL6
Sharps	Clino; Possibly Ortho	H3
Shaw	Ortho	L6
Soko Banja	Disordered Ortho	LL4
Tulia	Ortho	H5
Waconda	Ortho; Probably Disordered Ortho	L6

Ortho = Orthorhombic

Clino = Monoclinic

Table IV

Type of Pyroxene Crystals Found in Other Chondrites

Meteorite	Number of Crystals: Disordered Orthopyroxene	Ordered Orthopyroxene	Twinned Clinoenstatite	Twinned Clinoenstatite With Some Disordered Enstatite
Ochansk[1]	1	1		
Soko Banja	1			
Clovis			1	1
Hamlet			2	1
Chainpur			5	1
Coolidge			2	1
Parnallee		1		
Bjurbole		1		
Bremervörde		2		
Hallingeberg				

1. The Ochansk crystal contained some twinned clinopyroxene.

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Dodd, R. T., Jr. and Van Schmus, R., (1965). Significance of the Unequilibrated Ordinary Chondrites. J. of Geophys. Res., **70**, (16) 3801-3811.

Keil, K. and Fredriksson, K., (1964). The Iron, Magnesium and Calcium Distribution in Coexisting Olivines and Rhombic Pyroxenes of Chondrites. J. of Geophys. Res., **69**, 3487-3515.

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Pollack, S. S., and Ruble, W. D. (1964). X-ray Identification of Ordered and Disordered Orthoenstatite. Am. Miner., **49**, 983-992.

Van Schmus, W. R. and Wood, J. A., (1966). A Chemical-Petrologic Classification for the Chondritic Meteorites. Smithson Astro. Observ. Preprints in Meteorites, August.

Acknowledgements

Most of the meteorites were obtained from Dr. Brian Mason or from Dr. Carleton Moore and the Arizona State University Meteorite Collection.

Samples were kindly provided by Näykki, Kivimuseo, Helsinki, Finland (Huittinen), Dr. E. Olsen, Chicago Natural History Museum (Indarch), and S. Bagchi, Geological Survey of India (Kot Lalu).

Personnel

Dr. Sidney S. Pollack and Marianne Hoy spend half their time working on this contract.

Scientific Meeting

Dr. Pollack attended the Gordon Conference on "The Chemistry and Physics of Space", June 27 - July 1, 1966.

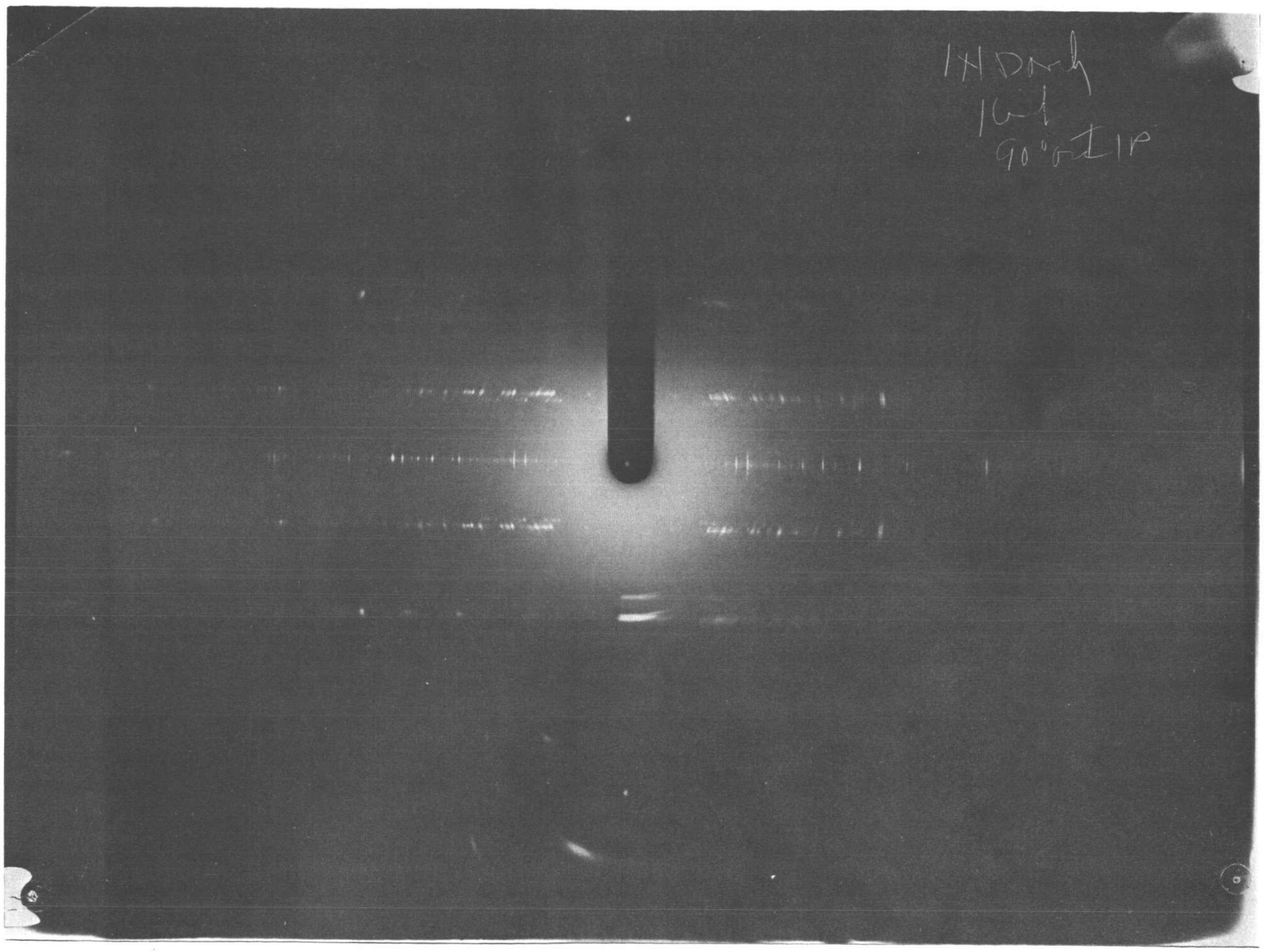

Figure 1. Oscillation photograph of crystal from Indarch. (Enstatite chondrite).

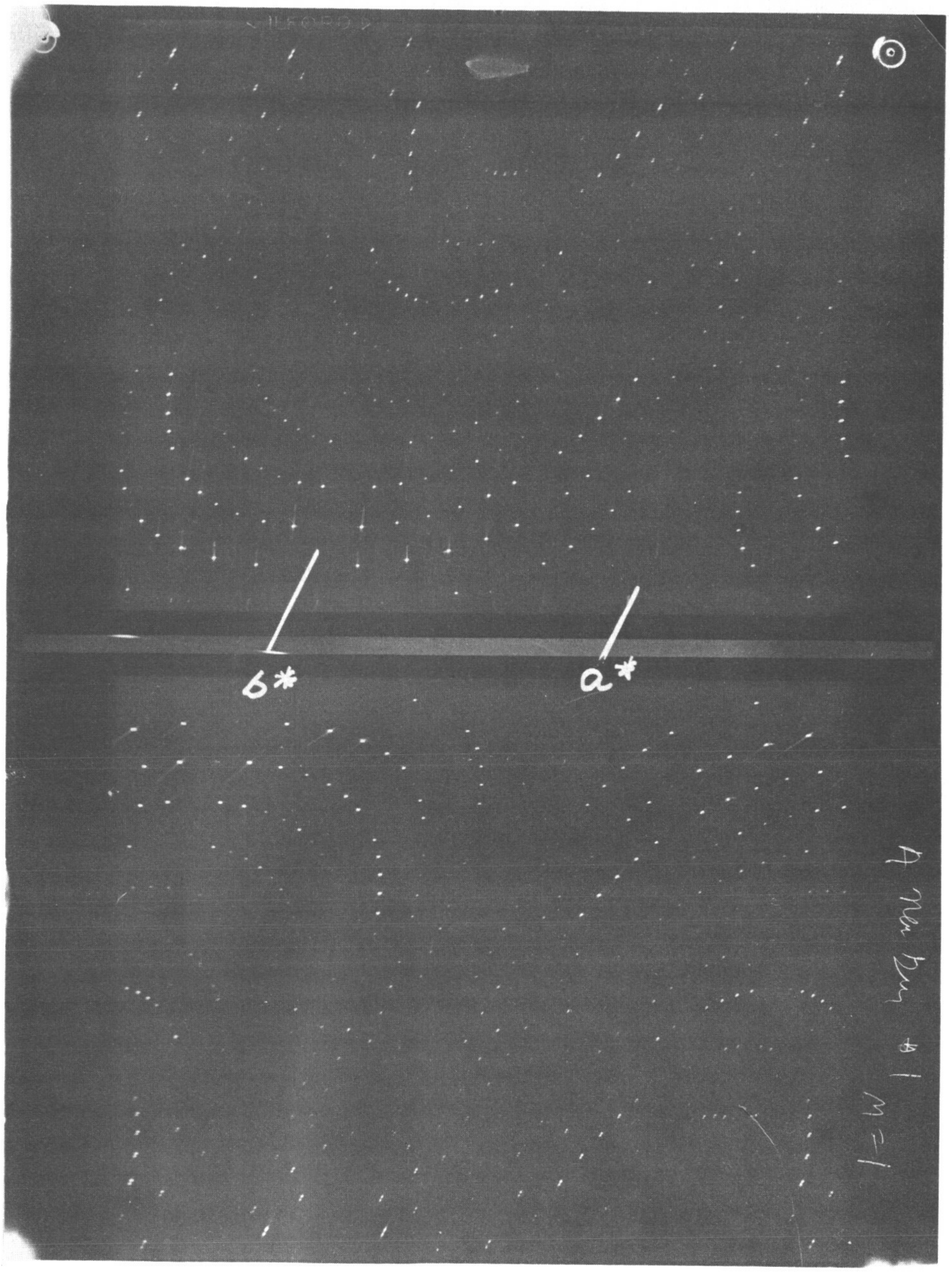

Figure 2. Weissenberg (hkl) net of an ordered enstatite crystal from New Guinea.

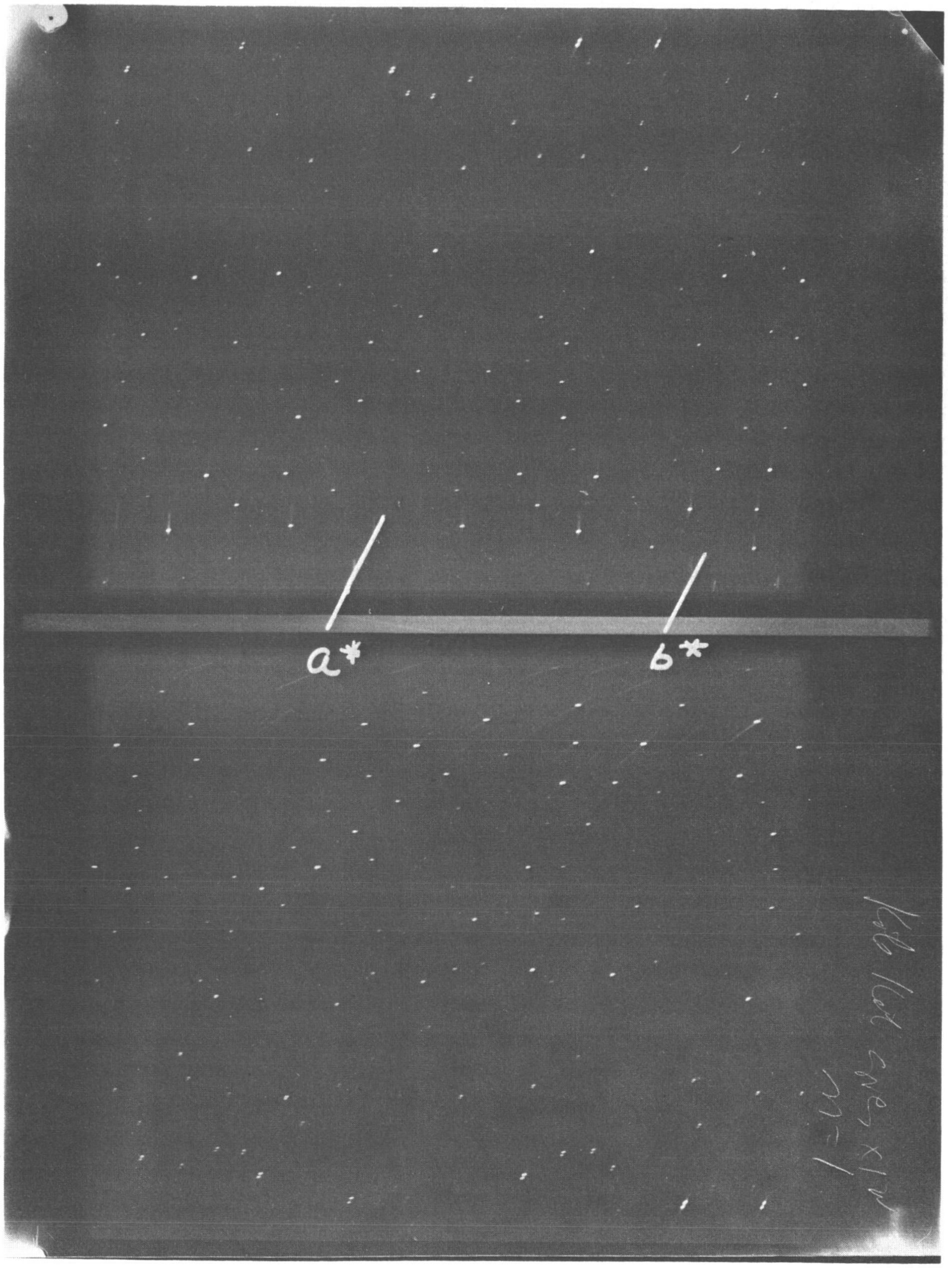

Figure 3. Weissenberg (hkl) net of untwinned clino pyroxene.

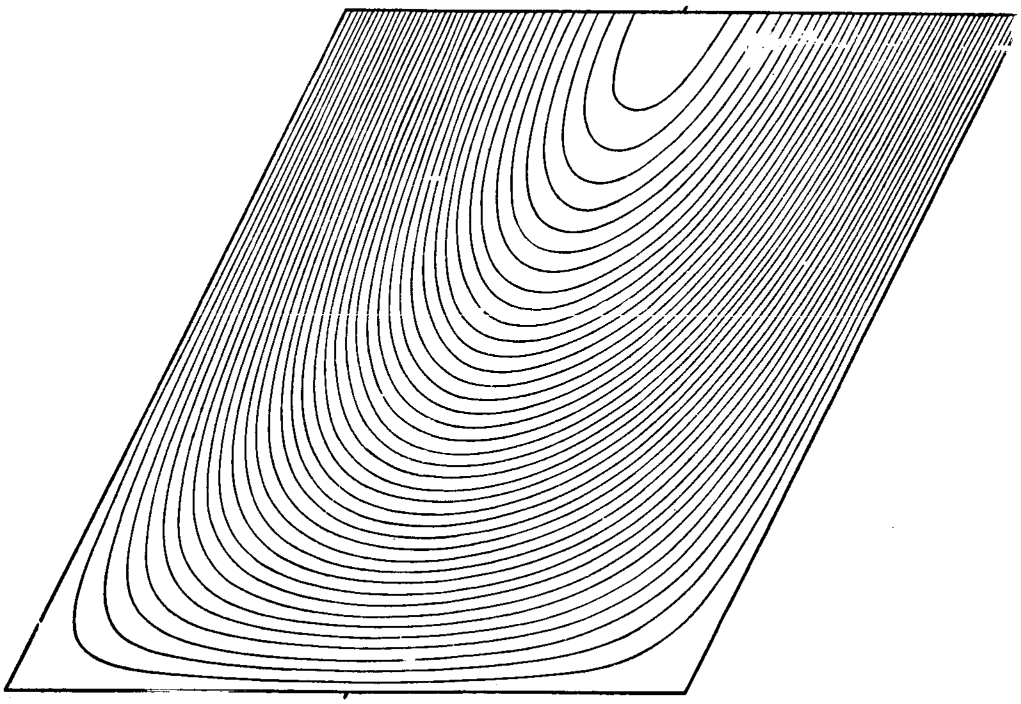

Figure 4a. Template used to indicate parallel lattice row lines for equi-inclination Weissenberg photographs. Reprinted from X-Ray Crystallography, M. J. Burger, John Wiley and Sons, 1942.

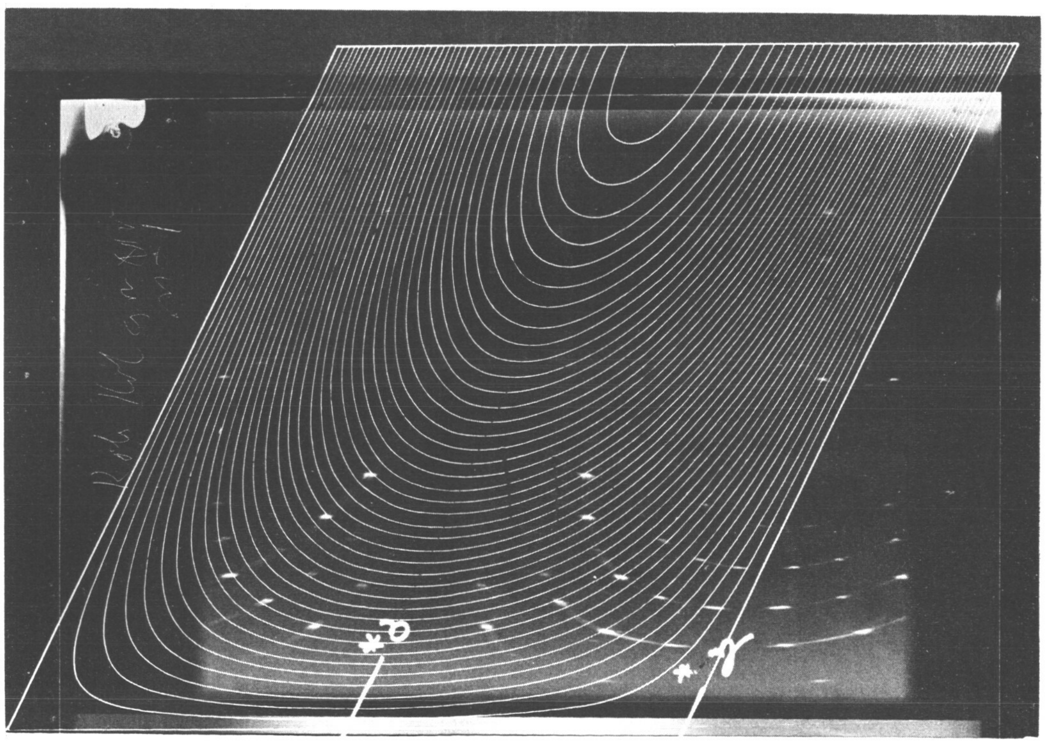

Figure 4b. Template from Figure 4 aligned to show festoons parallel to the $\underline{a}^*$ direction of an hkl net of a Kota-Kota crystal. (Enstatite chondrite).

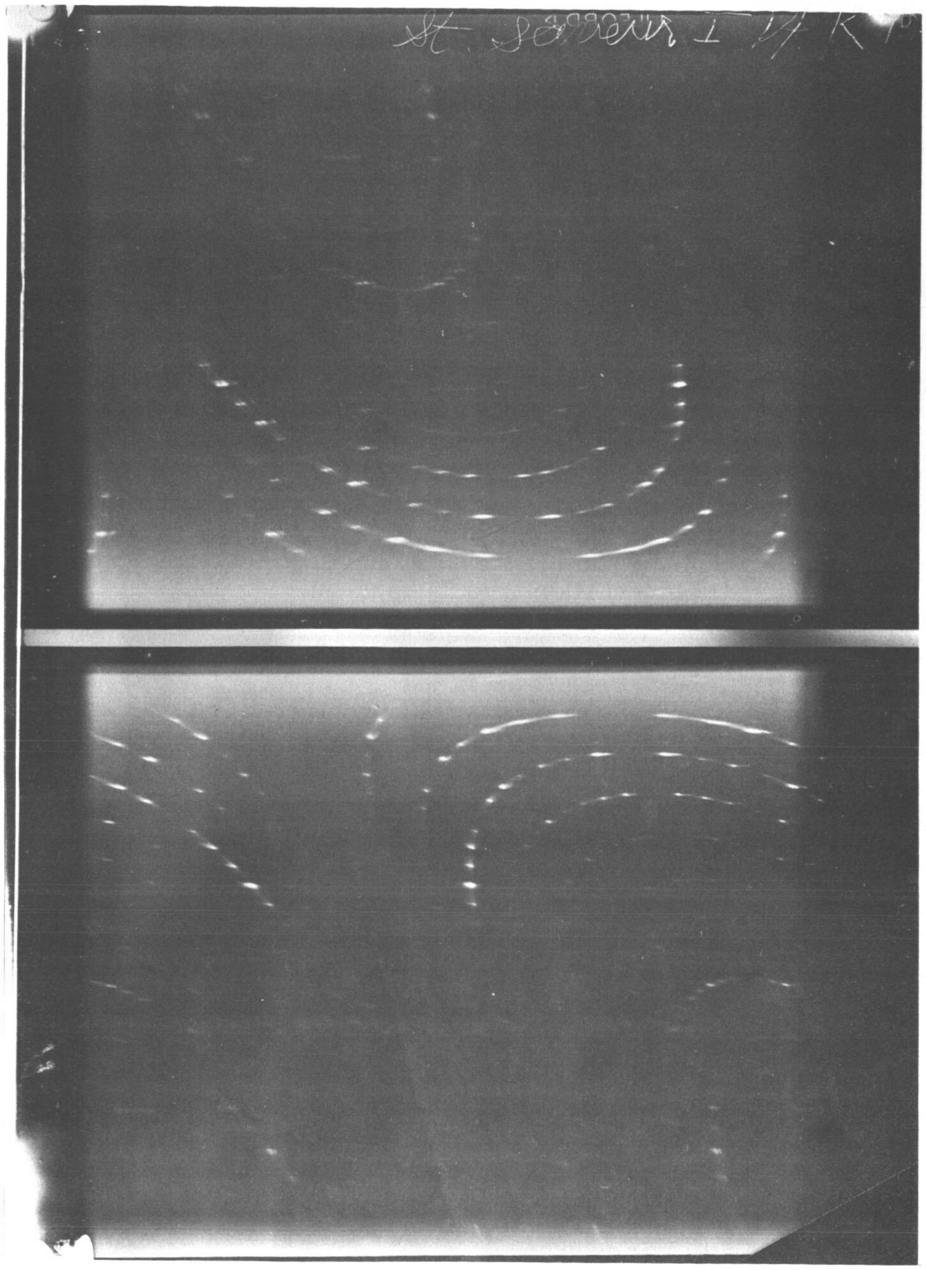

Figure 5. Weissenberg (hkl) net from a St. Sauveur crystal, showing ordered enstatite pattern plus streaks between spots along festoons parallel to a*. (Enstatite chondrite).

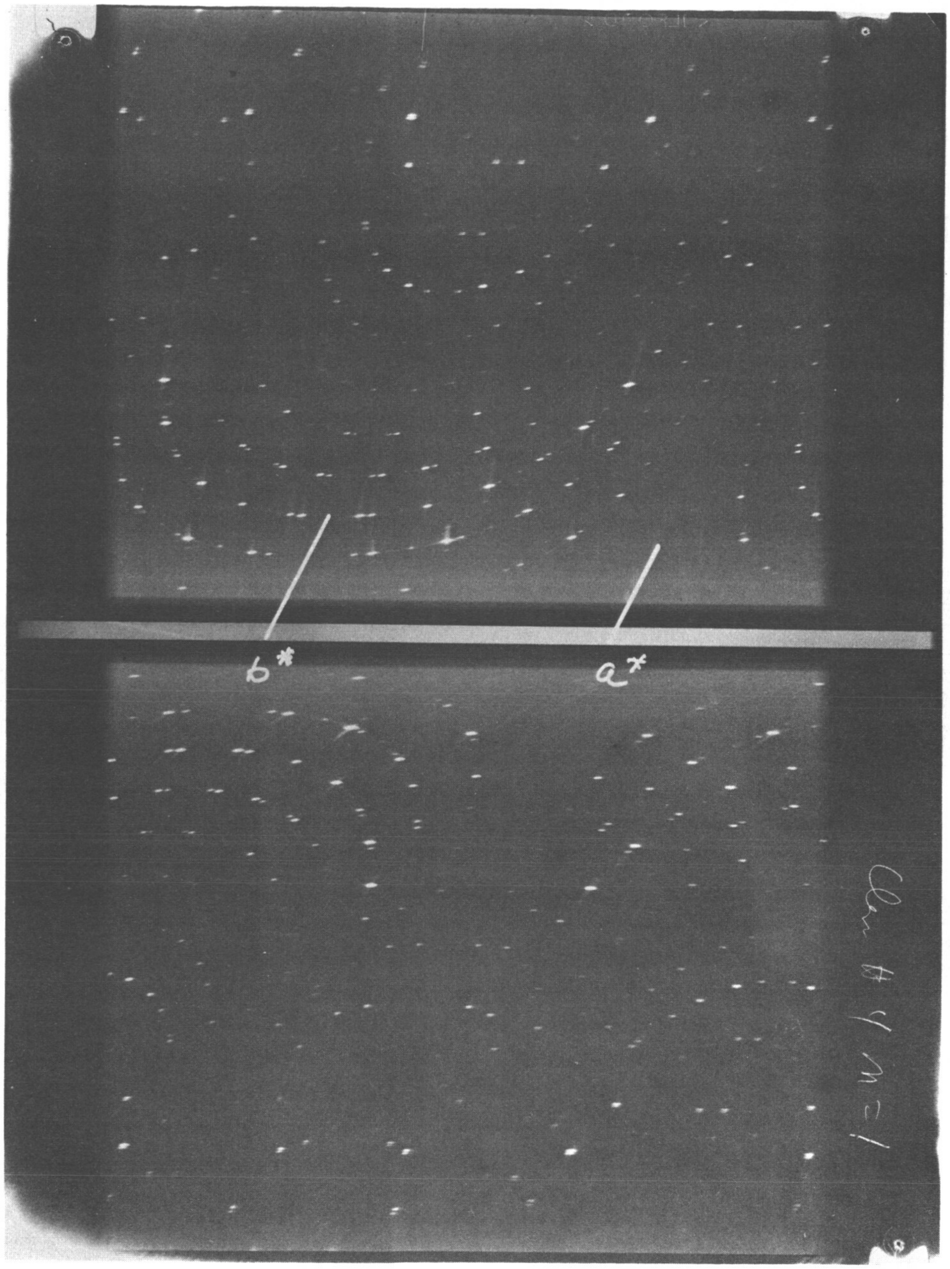

Figure 6. Weissenberg (hkl) net from New Guinea, twinned clinoenstatite crystal. Very weak streaks are present along festoons parallel to a*.

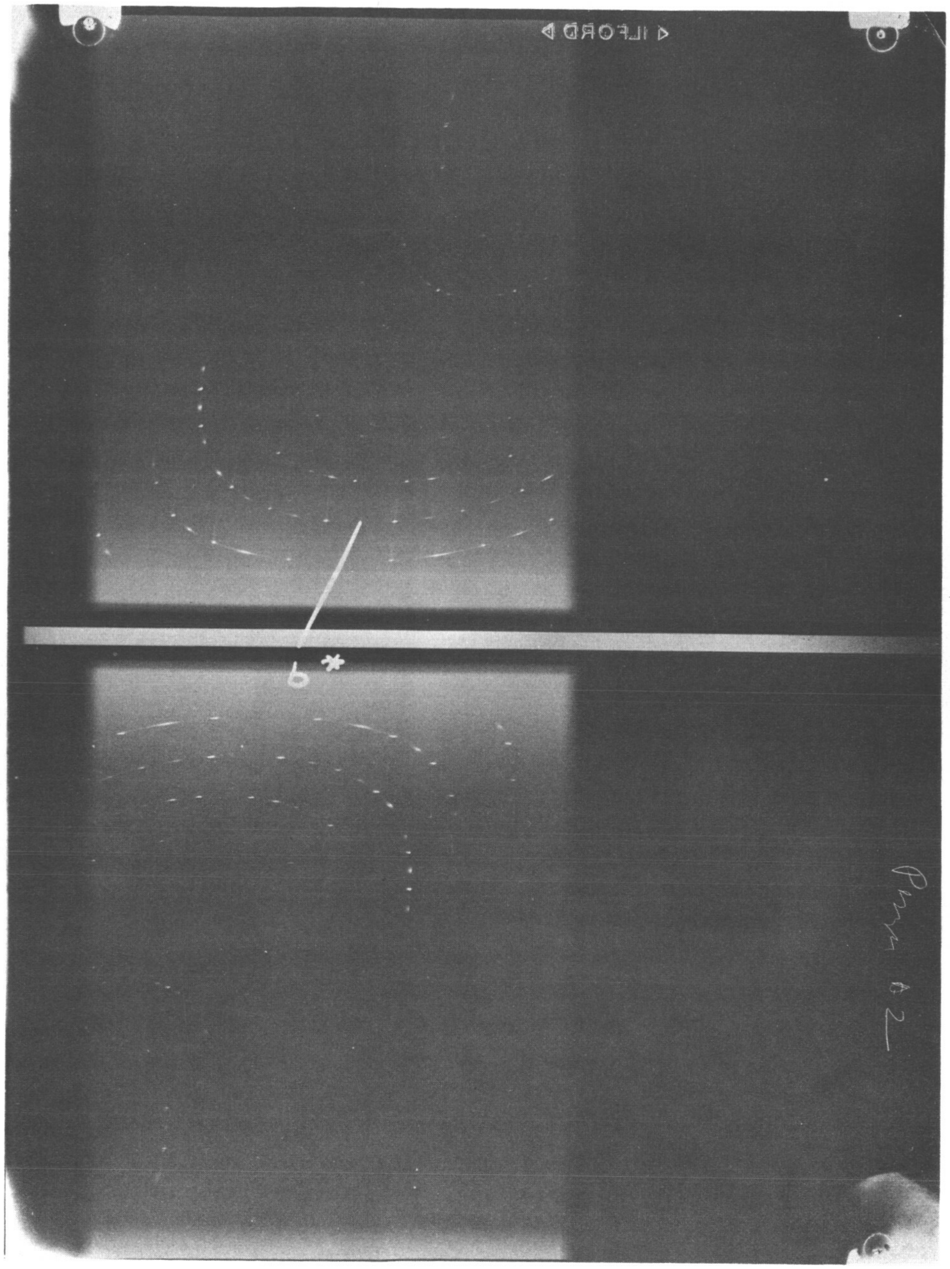

Figure 7. Weissenberg (hkl) net from Pesyanoe crystal. This pattern shows sharp spots when h is odd but diffuse spots for even values of h. (Enstatite achondrite).

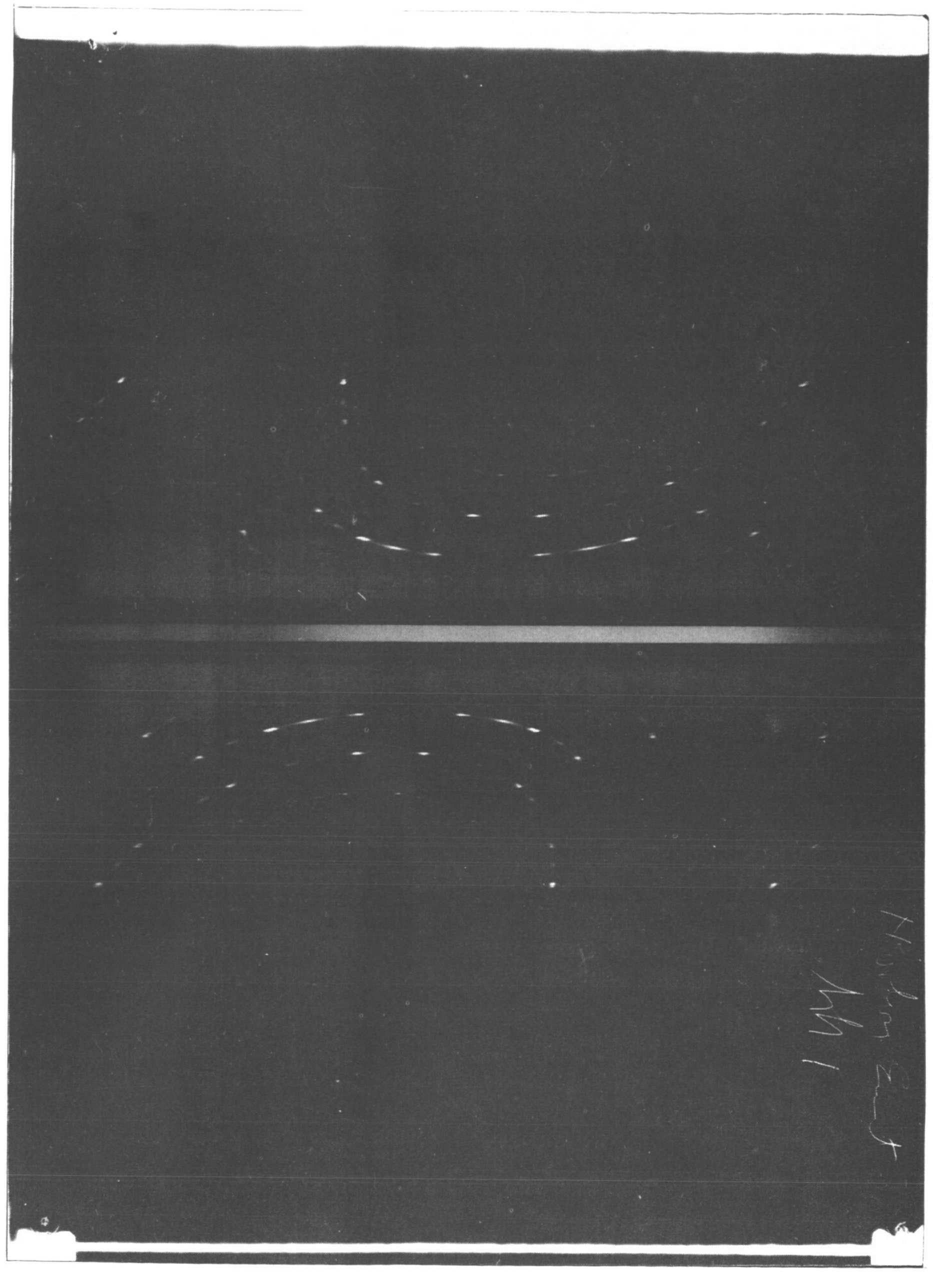

Figure 8. Weissenberg (hkl) net from Norton County crystal. This pattern contains sharp spots for odd values of h and diffuse spots for even values of h, similar to Figure 7. In addition, it contains spots due to twinned clinoenstatite. (Enstatite achondrite).

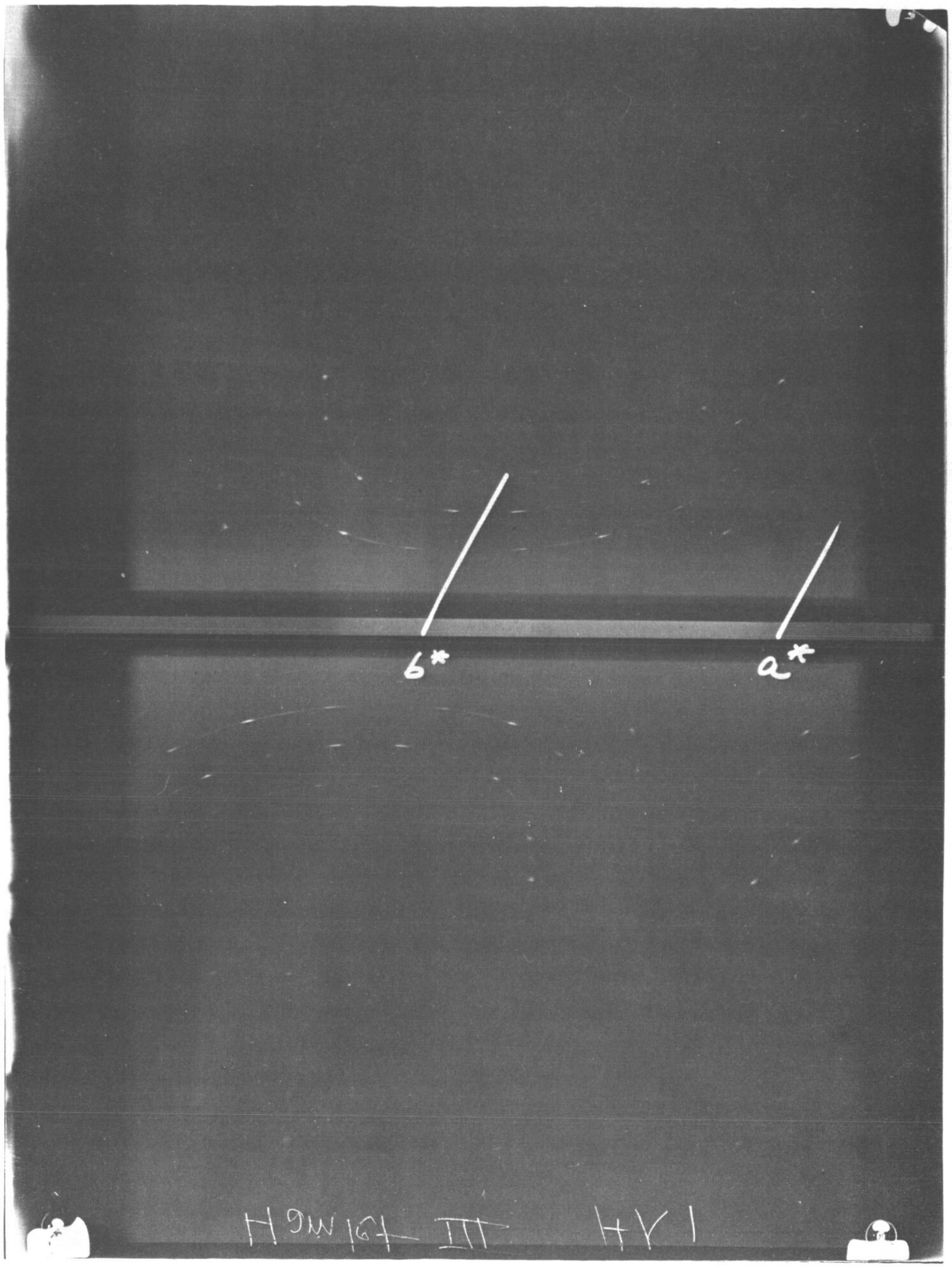

Figure 9. Weissenberg (hkl) net from Hamlet crystal. (Chondrite).