

*Unit cell volumes of synthetic orthoenstatite and low
clinoenstatite*

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Summary. Cell dimensions and densities derived from least-squares refinement of X-ray powder diffractometer patterns are: orthoenstatite, a 18.2249 ± 0.0013 , b 8.8149 ± 0.0008 , c 5.1746 ± 0.0008 Å, V 831.30 ± 0.14 Å³, D 3.208 g/cc; low clinoenstatite, a 9.6065 ± 0.0011 , b 8.8146 ± 0.0007 , c 5.1688 ± 0.0006 Å, $\beta = 108.335 \pm 0.009$, $V = 415.46 \pm 0.09$ Å³, D 3.210 gm/cc. Because orthoenstatite transforms reversibly to clinoenstatite at high pressure and low temperature, and because a statistical test shows that orthoenstatite is less dense than clinoenstatite at the 90 % confidence level (in accord with the direction of slope of the experimental transition curve), it is no longer possible to regard low clinoenstatite as a metastable form of MgSiO₃.

RECENT attempts to clarify the complex data on the polymorphism of MgSiO₃ (Brown and Smith, 1963; Boyd and Schairer, 1964) concluded that at atmospheric pressure protoenstatite is stable at high temperature, and clinoenstatite is a metastable phase produced by quenching protoenstatite in the stability field of orthoenstatite. Brown, Morimoto, and Smith (1961) presented crystal-chemical arguments implying that smaller atomic displacements are needed to form clinoenstatite instead of orthoenstatite from protoenstatite, thus explaining the metastable formation of clinoenstatite during quenching. Recent syntheses by Sclar, Carrison, and Schwartz (1964) have demonstrated a reversible phase boundary between clinoenstatite on the higher-pressure–lower-temperature side and orthoenstatite at the lower-pressure–higher-temperature side. They report that the phase boundary is given by $T(^{\circ}\text{C}) = 538 + 3.3P$ (kilobars). Davis (1963), Boyd and England (1963), and Boyd, England, and Davis (1964) have synthesized MgSiO₃ polymorphs between 1300 and 1950° C and pressures up to 46 Kb. Protoenstatite is stable from about 1000° C to the melting point at atmospheric pressure, but at pressures above 8 Kb and temperatures above 1300° C orthoenstatite is the only phase present. At pressures below 8 Kb an

equilibrium phase boundary apparently exists between orthoenstatite and protoenstatite. Lindsley and Boyd (1965) have confirmed the orthoenstatite-clinoenstatite transition and have found there is an analogous transition in FeSiO_3 . These results from controlled syntheses give a rather complete P - T diagram in which the stability fields of all three polymorphs are defined. Perrotta and Stephenson (1965) have discovered a rapid high-low inversion in metastable clinoenstatite at 995°C and atmospheric pressure.

The experimentally determined positive slope (dP/dT) of the boundary between orthoenstatite and clinoenstatite requires that clinoenstatite is denser than orthoenstatite, but some of the more reliable literature values for the density indicate the opposite (table I). Direct determination of density is difficult because of the ubiquitous presence of impurities and structural defects, while indirect estimation from cell dimensions has been complicated by the possible presence of Fe, Ca, and Al as significant substituents, and by low experimental accuracy. Consequently, we have accurately indexed X-ray powder patterns of ultra-pure synthetic orthoenstatite and clinoenstatite in an attempt to demonstrate conclusively which form is denser.

Synthesis of MgSiO_3 samples. The orthoenstatite and clinoenstatite used in the X-ray determinations were prepared by reacting equimolar mixtures of Mallinckrodt ultrapure MgO (99.99 %) and Davison grade 923 silica gel, which contains about 17 % water and less than 0.05 % impurities. The samples were enclosed in $\frac{1}{8}$ in. diameter platinum tubes and held at the appropriate P - T conditions in a belt pressure apparatus.

Orthoenstatite was synthesized at 62 Kb and 930°C for three hours, in its stability field. It had α 1.650, β 1.652, γ 1.658, all ± 0.001 (Na light); $2V_\gamma$ (calc.) 60° . These data may be compared with those given by Foshag (1940) for orthoenstatite from the Shallowater, Texas, meteorite: α 1.653, β 1.656, γ 1.660, $2V_\gamma$ (calc.) 54.5° . The latter data are commonly used to represent the properties of pure orthoenstatite in optical properties *vs.* composition diagrams despite the presence of 0.38 % FeO and 0.32 % CaO in the Shallowater orthoenstatite. Winchell (1933) gave the optical properties of pure artificial orthoenstatite in exact accord with our sample, but these data are not cited in Winchell and Winchell (1951). The refractive indices of orthoenstatite from the Bishopville, South Carolina, meteorite are reported to be α 1.650, β 1.653, γ 1.658, all ± 0.003 (Allen, Wright, and Clement, 1906) or α 1.649, β 1.653, γ 1.658 (Swanson *et al.*, 1956). This material has been widely used as a source of pure orthoenstatite, but it reportedly contains 0.1 to 1.0 % each of Al.

TABLE I. Comparison of the densities of orthoenstatite and low clinoenstatite

	<i>Orthoenstatite</i>	<i>D_{obs.}</i>	<i>D[*] calc.</i>	<i>Low clinoenstatite</i>	<i>D_{obs.}</i>	<i>D[*] calc.</i>
Bishopville meteorite (Morimoto, 1959)		—	3-205	Synthetic low clinoenstatite (Allen, Wright, and Clement, 1906)	3-192	—
Bishopville meteorite (Swanson <i>et al.</i> , 1956)		—	3-194	Heated Bishopville meteorite (Morimoto <i>et al.</i> , 1960)	—	3-190
Bishopville meteorite (Pollack and Ruble, 1964)		—	3-204	Synthetic low clinoenstatite (Kuno and Hess, 1953)	—	3-191
Shallowater meteorite (Hess, 1952)		3-209	3-210	Synthetic low clinoenstatite (Winchell, 1931 and Winchell and Winchell, 1951)	3-19	—
Synthetic orthoenstatite (?) (Winchell, 1933)		3-18	—	Synthetic low clinoenstatite (Lindemann, 1956)	—	3-182
Synthetic orthoenstatite (?) (Allen, Wright, and Clement 1906)		3-175	—	Synthetic low clinoenstatite (this study)	—	3-210
Synthetic orthoenstatite (Atlas, 1952)		—	3-170			
Synthetic orthoenstatite (Greenwood, 1963)		—	3-200			
Synthetic orthoenstatite (this study)		—	3-208			

* All calculated densities except that for the Shallowater meteorite are based on the assumption that the samples are pure MgSiO₃.

Ca, and Fe as well as 0.01 to 0.1 % each of Cr, Mn, Na, and Ti (Swanson *et al.*, 1956).

Clinoenstatite was synthesized at 75 Kb and 700° C for two hours in the stability field of low clinoenstatite. The sample is largely granular but in part acicular. There appears to be a pressure-dependent habit variation of low clinoenstatite in the temperature range 550 to 750° C. Below 70 Kb, it is dominantly acicular; above 70 Kb, it is dominantly granular. The γ index of refraction of this sample is 1.660 ± 0.001 (Na light) and is definitely higher than that of orthoenstatite. It is very difficult to make accurate measurements of the α and β refractive indices because the crystals are either too small or twinned polysynthetically. The γ index is in agreement with the optical data given by Winchell (1931, 1933) and Winchell and Winchell (1951) for synthetic low clinoenstatite: α 1.651, β 1.654, γ 1.660. The X-ray diffraction pattern shows one weak reflection at 3.08 Å not ascribable to low clinoenstatite. This is probably the strongest reflection of coesite, a small amount of which was observed microscopically. This reflection was omitted from the powder data.

X-Ray data. To ensure the greatest possible precision a new Philips wide-range X-ray diffractometer and supporting circuitry were utilized in order to take advantage of unworn mechanical parts and more sensitive electronics. When the instrument had been properly aligned, all diffraction maxima of the Philips silicon standard fell within $\pm 0.005^\circ 2\theta$ of their calculated values from $20^\circ 2\theta$ to $100^\circ 2\theta$. Samples of orthoenstatite and low clinoenstatite were then mounted on glass slides without a binder and pressed flat. Each glass slide was adjusted with metal shims to ensure that the sample surface was tangential to the focusing circle.

Preliminary scans of both samples at $\frac{1}{4}^\circ 2\theta$ per minute at various scale factors established the approximate positions of all diffraction maxima. Before mixing a spinel internal standard (itself calibrated with spectroscopically pure Si, a 5.43062 Å) with each sample, peaks near spinel lines were scanned at $\frac{1}{8}^\circ 2\theta$ per minute several times to permit their location relative to peaks not obscured by spinel lines. After addition of the spinel standard, the shims were adjusted so that all spinel diffraction maxima fell within $0.005^\circ 2\theta$ of their calculated positions. In this manner, errors arising from making a slightly wrong correction for sample peak positions relative to theoretical spinel peak positions could be minimized. Frequent checks of the spinel peaks were made to ensure that the sample remained in good alignment. Peak positions were determined at two-thirds the peak height because many peaks were too closely spaced to permit peak centroids to be determined. Integrated intensities were obtained by measurement with a polar planimeter. After averaging peak positions from several scans made at $\frac{1}{8}^\circ 2\theta$ per minute, individual maxima were profiled by counting at increments of $0.01^\circ 2\theta$. This practice was abandoned after about 25 values obtained by step scanning were found to agree closely with peak positions read from the chart recorder. Filtered copper radiation was used throughout since many weak diffractions were obscured by background noise when an attempt was made to utilize iron radiation. With the aid of pulse height analysis, peak to background ratios were substantially increased so that every line less than $90^\circ 2\theta$ present on a standard Debye-Scherrer film was recorded by the instrument. Because a few faint lines in the back-reflection region were observed on Debye-

Scherrer films but were not detected by the diffractometer, an effort was made to locate them accurately by the use of a Jagodzinski semi-focusing camera operated in the positive asymmetric back reflection mode. Films thus obtained were not of sufficient quality to provide any additional data.

When all observable diffraction maxima were recorded with an estimated error no greater than $\pm 0.01^\circ 2\theta$ and for most lines within $\pm 0.005^\circ 2\theta$, refinement of the powder data was begun. By means of a computer programme, initial cell parameters

TABLE II. Powder data of orthoenstatite using filtered copper radiation (λ 1.5418, 1.54050). W , weighting factor; in the third scheme of weighting, lines were weighted inversely as these factors

hkl	$d_{obs.}$	$d_{calc.}$	W	I/I_0	hkl	$d_{obs.}$	$d_{calc.}$	W	I/I_0
210	6.3300 Å	6.3357 Å	10	4	702	1.8342	1.8352	2	1
020	4.4110	4.4074	4	19	10.1.0	1.7849	1.7847	1.5	5
121	3.2998	3.2999	4	9	541	1.7697	1.7718	2	2
420	3.1677	3.1678	3	74	250	1.7308	1.7309	1.5	5
221	3.1502	3.1486	3	49	831	1.6995	1.7004	2	2
321	2.9359	2.9371	10	2	812	1.6785	1.6785	2	1
610	2.8705	2.8718	2	100	023	1.6062	1.6062	2	1
511	2.8219	2.8229	3	7	10.2.1	1.6014	1.6015	2	1
230	2.7961	2.7965	10	2	902	1.5948	1.5946	2	1
421	2.7017	2.7018	3	8	931	1.5868	{1.5870	100}	3
131	2.6299	2.5304	2	18	413}		{1.5868	100}	
202	2.4899	2.4889	3	7	840	1.5833	1.5839	2	2
521	2.4681	2.4686	2	11	650	1.5253	1.5248	1.5	4
302	2.3779	2.3804	5	1	12.0.0	1.5185	1.5187	1	14
331	2.3528	2.3553	5	1	10.3.1	1.4839	1.4837	1	19
800	2.2772	2.2781	3	7	060	1.4696	1.4691	1	24
402	2.2478	2.2499	4	1	352	1.4169	1.4167	1	1
431	2.2286	2.2286	3	2	11.0.2}		{1.3953	100}	1
630	2.1105	2.1119	1.5	7	850 }	1.3950	{1.3942	100}	
531	2.0919	2.0922	1.5	11	11.3.1	1.3904	1.3901	1	6
721	2.0570	2.0569	2	2	12.3.1	1.3060	1.3055	1	5
512	2.0513	2.0519	2	2	12.1.2	1.2957	1.2955	2	2
820	2.0230	2.0238	2	2	14.1.0	1.2876	1.2878	1.5	3
141	2.0136	2.0151	3	2	214 }		{1.2675	100}	2
440	1.9823	1.9839	1.5	4	10.5.0}	1.2670	{1.2671	100}	
241	1.9782	1.9791	1.5	4	304	1.2656	1.2653	2	2
631	1.9548	1.9553	1	9	16.0.0	1.1392	1.1390	2	1
821	1.8841	1.8847	2	2	12.6.0	1.0561	1.0559	1.5	3
332	1.8499	1.8496	2	1	14.5.0	1.0472	1.0472	1.5	3

averaged from literature values were used to generate all possible hkl indices and corresponding d -values down to a minimum of 1.0 Å. Low angle lines were assigned indices most of which were unambiguous; i.e. only one hkl per line. When about twenty unambiguous lines had been established for each sample, an initial least squares refinement of cell parameters was performed to arrive at a more accurate estimate of the cell parameters. The values obtained were in turn used to generate new hkl indices and corresponding d -values permitting additional higher angle lines to be indexed. Three cycles of this procedure allowed accurate indexing of all lines. In the higher 2θ regions, many peaks corresponded to several calculated diffractions, so further elimination of possible indices was carried out on the basis of observed and calculated structure factors. Possible diffractions of the orthoenstatite pattern that were weak or unobserved on Weissenberg and precession films of a single crystal of orthoenstatite (Bishopville meteorite) were deleted from the list. This resulted in the indexing for orthoenstatite shown in table II. A similar elimination of possible

diffractions from the low clinoenstatite pattern was accomplished by calculation of structure factors from the atomic coordinates given by Morimoto, Appleman, and Evans (1960) and deletion of those with low $|F|^2$ values. This gave the indexing shown in table III.

TABLE III. Powder data of low clinoenstatite using filtered copper radiation. W , weighting factor (see table II)

hkl	$d_{obs.}$	$d_{calc.}$	W	I/I_0	hkl	$d_{obs.}$	$d_{calc.}$	W	I/I_0
110	6.3391 Å	6.3377 Å	100	1	242	1.6567	1.6575	1.5	1
020	4.4089	4.4073	10	5	31 $\bar{2}$	1.6401	1.6403	1	3
011	4.2888	4.2867	100	1	531	1.6055	1.6060	1	12
11 $\bar{1}$	3.5229	3.5244	100	1	440 } 34 $\bar{1}$ }	1.5850	{ 1.5844 1.5853 }	{ 100 100 }	1
021	3.2808	3.2786	4	24	350	1.5244	1.5249	1	7
220	3.1699	3.1686	4	31	600	1.5203	1.5198	1	10
221	2.9756	2.9747	2	76					
310	2.8732	2.8736	2	100	233	1.4852	1.4849	1	6
130	2.7936	2.7966	10	1	133	1.4752	1.4751	2	1
21 $\bar{1}$	2.7633	2.7660	10	1	060	1.4691	1.4691	1.5	4
131	2.5376	2.5372	2	14	40 $\bar{2}$	1.4570	1.4569	2	1
202	2.5176	2.5154	2	18	35 $\bar{1}$ }	1.3943	{ 1.3952 1.3933 }	{ 100 100 }	1
002	2.4524	2.4530	2	28	523 }				
22 $\bar{1}$	2.4313	2.4306	2	17					
231	2.3737	2.3745	2	8	243 }	1.3563	{ 1.3563 1.3558 }	{ 100 100 }	2
302	2.2928	2.2939	10	1	133 }				
400	2.2777	2.2797	10	1	702	1.3382	1.3380	2	1
040	2.2066	2.2036	2	5	712	1.3230	1.3228	2	1
10 $\bar{2}$	2.2015	2.2014	2	5	043 }	1.3134	{ 1.3132 1.3137 }	{ 100 100 }	1
11 $\bar{2}$	2.1362	2.1358	5	2	533 }				
331	2.1152	2.1156	1.5	30	304 }	1.2873	{ 1.2865 1.2887 }	{ 100 100 }	1
421	2.0882	2.0888	5	1	262 }	1.2686	{ 1.2686 1.2696 1.2684 }	{ 100 100 100 }	1
322	2.0312	2.0348	5	1	51 $\bar{2}$ }				
402	2.0157	2.0158	2	4	31 $\bar{3}$ }				
041	2.0106	2.0102	2	4	062	1.2604	1.2604	2	1
240	1.9831	1.9841	3	1	731	1.2423	1.2421	2	1
412	1.9648	1.9650	3	1	014 }	1.2151	{ 1.2148 1.2150 }	{ 100 100 }	1
241	1.9328	1.9336	3	2	353 }				
20 $\bar{2}$	1.9220	1.9225	3	1	35 $\bar{2}$	1.2123	1.2121	1.5	2
431	1.8454	1.8457	3	1	36 $\bar{2}$	1.1033	1.1028	2	1
510	1.7852	1.7859	1.5	4	752	1.0658	1.0658	2	1
22 $\bar{2}$	1.7618	1.7622	1	8	281	1.0632	1.0628	2	1
24 $\bar{1}$ }	1.7580	{ 1.7576 1.7585 }	{ 100 100 }	8	750	1.0478	1.0477	2	1
521 }					304 }	1.0307	{ 1.0304 1.0306 }	{ 100 100 }	1
150	1.7305	1.7309	2	4	28 $\bar{1}$ }				
42 $\bar{1}$	1.7110	1.7107	2	1					

To determine the effect of different ways of weighting the observations on the cell parameters, various schemes were used in the final refinements. Table IV shows the results obtained when (1) all lines were processed with equal weight, (2) only unambiguous lines above $50^\circ 2\theta$ were used, or (3) all lines were weighted according to intensity, diffraction angle (2θ), and ambiguity. The weights (W) used in the last scheme are shown in tables II and III. It is evident that some systematic error is responsible for the variation in cell parameters for the three weighting schemes. For a discussion of systematic errors in powder diffractometry,

the reader is referred to Parrish, Taylor, and Mack (1964). Because of the complexity of the present powder patterns, it was not feasible to apply correction factors depending on spectral distribution, axial dispersion, absorption, etc. Although an internal standard was used in an attempt

TABLE IV. Cell parameters (in Å) and their standard deviations at 26° C.

	Weighting scheme	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>V</i>
Orthoenstatite	1	18.2251	8.8143	5.1737	—	831.10
		± 0.0016	± 0.0010	± 0.0007		± 0.13
	2	18.2259	8.8167	5.1754	—	831.65
		± 0.0010	± 0.0008	± 0.0006		± 0.10
	3	18.2249	8.8149	5.1746	—	831.30
		± 0.0013	± 0.0008	± 0.0008		± 0.14
Low clinoenstatite	1	9.6048	8.8148	5.1698	108.345	415.45
		± 0.0015	± 0.0010	± 0.0007	± 0.011	± 0.11
	2	9.6069	8.8165	5.1688	108.339	415.56
		± 0.0017	± 0.0009	± 0.0010	± 0.013	± 0.14
	3	9.6065	8.8146	5.1688	108.335	415.68
		± 0.0011	± 0.0007	± 0.0006	± 0.009	± 0.09
Orthoferrosilite	—	18.431	9.080	5.238	—	876.68
						± 0.54
Clinoferrosilite	—	9.7085	9.0872	5.2284	108.432	437.60
						± 0.12

Data for orthoferrosilite and clinoferrosilite kindly supplied by C. W. Burnham of the Geophysical Laboratory of the Carnegie Institution of Washington.

to eliminate such factors, it is possible that compensation was not complete. The high-angle lines for both forms of enstatite were rather broad, rendering difficult the measurement of the peak positions. The source of the broadening is not known. Disorder (Brown and Smith, 1963) is one possibility, but our data for synthetic orthoenstatite are not in accord with the criteria for disordered enstatite given by Pollack and Ruble (1964). Optical examination showed that the crystals are large enough to eliminate particle-size line broadening unless the crystals are composed of a mosaic of very small units. Perhaps during release of pressure after crystal synthesis, the crystals are stressed resulting in internal break-up without change of external morphology. Annealing for five hours at 800° C produced no sharpening of the diffraction pattern. The average error in the cell parameters listed in table IV is about 1 in 10⁴.

The reader is referred to Deming (1943) and Burnham (1961) for a detailed description of the calculation of the error in the cell volumes. Briefly, the estimated variance (σ^2) in volume is given by $\xi \cdot c \cdot \xi$, where

ξ is the column vector $\{\partial V/\partial a \ \partial V/\partial b \ \partial V/\partial c\}$ and \mathbf{c} the covariance matrix of the observed values of a , b , and c . For the present purpose it is important to realize that this estimate of error depends principally on the random error of measurement and on uncertainties caused by small displacements of peak positions by overlapping. Assuming that systematic errors are the same for both polymorphs, it is possible to test the hypothesis that clinoenstatite is denser by use of the standard equation $t = \Delta V/(\hat{\sigma}_1^2 + \hat{\sigma}_2^2)^{1/2}$. Using the large sample approximation, the confidence levels for the hypothesis to be true are: refinement scheme 1, 60 %; scheme 2, 90 %; scheme 3, 90 %. The third weighting scheme is preferred because it is based on a reasoned judgment of the errors for individual lines. Even for this scheme, the confidence level is only moderate.

Density of MgSiO₃ polymorphs based on the Gladstone-Dale relationship. The general applicability of the Gladstone-Dale relationship, $(n-1)/d$, where $n = \sqrt[3]{\alpha\beta\gamma}$ and $d =$ density, has been demonstrated by Jaffe (1956). Using the optical constants for our synthetic orthoenstatite and the optical constants for synthetic low clinoenstatite given by Winchell and Winchell (1951) plus the specific refractive energies for MgO and SiO₂ given by Larsen and Berman (1934), the calculated densities for orthoenstatite and low clinoenstatite are 3.20 and 3.21, respectively.

Conclusions. All three lines of evidence—slope of the orthoenstatite-clinoenstatite phase boundary, densities, and refractive indices—lead to the conclusion that clinoenstatite is denser than orthoenstatite, and this convergence helps to give confidence to the proposition that clinoenstatite is the stable, low-temperature form of MgSiO₃. Similar evidence leads to the conclusion that clinoferrosilite is the stable, low-temperature form of FeSiO₃. Because orthopyroxene is the ubiquitous form of (Mg,Fe)SiO₃ in metamorphic and plutonic environments, while the clino-equivalent (pigeonite) appears to form at high temperatures and to invert to an orthopyroxene (plus augite) at low temperatures, there seems to be a drastic difference in stability for the end members and the intermediate compositions. The present results show that the cell volumes of orthoenstatite and clinoenstatite are extremely similar and it is possible that even small amounts of impurities such as Ca, Al, and Mn will cause major changes in the stability fields of the polymorphs. The lower symmetry of the clino- form of pyroxene may permit for atomic substitution quite different changes in coordination compared to the ortho-form. Finally, it should be emphasized that an unknown systematic error may occur in addition to the errors quoted in the text.

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References

- ALLEN (E. T.), WRIGHT (F. E.), and CLEMENT (J. K.), 1906. *Amer. Journ. Sci.*, ser. 4, vol. 22, p. 385.
- ATLAS (L.), 1952. *Journ. Geol.*, vol. 60, p. 125.
- BOYD (F. R.) and ENGLAND (J. L.), 1963. *Carnegie Inst. Washington Year Book*, vol. 62, p. 118.
- and SCHAIREEB (J. F.), 1964. *Journ. Petrology*, vol. 5, p. 275.
- , ENGLAND (J. L.), and DAVIS (B. T. C.), 1964. *Journ. Geophys. Res.*, vol. 69, p. 2101.
- BROWN (W. L.) and SMITH (J. V.), 1963. *Zeitschr. Krist.*, vol. 118, p. 186.
- , MORIMOTO (N.), and SMITH (J. V.), 1961. *Journ. Geol.*, vol. 69, p. 609.
- BURNHAM (C. W.), 1961. *Carnegie Inst. Washington Year Book*, vol. 61, p. 134.
- DAVIS (B. C. T.), 1963. *Ibid.*, vol. 62, p. 103.
- DEMING (W. E.), 1943. *Statistical adjustment of data*, chapters 3 and 9. John Wiley, New York.
- FOSHAG (W. F.), 1940. *Amer. Min.*, vol. 25, p. 779.
- GREENWOOD (H. J.), 1963. *Journ. Petrology*, vol. 4, p. 317.
- HESS (H. H.), 1952. *Amer. Journ. Sci.*, Bowen vol., p. 173.
- JAFFE (H. W.), 1956. *Amer. Min.*, vol. 41, p. 757.
- KUNO (H.) and HESS (H. H.), 1953. *Amer. Journ. Sci.*, vol. 251, p. 741.
- LARSEN (E. S.) and BERMAN (H.), 1934. *U.S. Geological Survey, Bull.* 848, p. 30.
- LINDEMANN (W.), 1956. *Geol. Bl. Nordost-Bayern*, vol. 6, p. 118.
- LINDSLEY (D. H.) and BOYD (F. R.), 1965. *Abstr. in Trans. Amer. Geophys. Union*, vol. 46, p. 181.
- MORIMOTO (N.), 1959. *Carnegie Inst. Washington Year Book*, vol. 58, p. 197.
- , APPLEMAN (D. E.), and EVANS (H. T.), 1960. *Zeitschr. Krist.*, vol. 114, p. 120.
- PARRISH (W.), TAYLOR (J.), and MACK (M.), 1964. *Advances in X-Ray Analysis*, vol. 7. Plenum Press, New York.
- PERROTTA (A. J.) and STEPHENSON (D. A.), 1965. *Science*, vol. 148, p. 1090.
- POLLACK (S. S.) and RUBLE (W. D.), 1964. *Amer. Min.*, vol. 49, p. 983.
- SCLAR (C. B.), CARRISON (L. C.), and SCHWARTZ (C. M.), 1964. *Abstr. in Trans. Amer. Geophys. Union*, vol. 45, p. 121.
- SWANSON (H. E.), GILFRIE (N. T.), and COOK (M. I.), 1956. *Nat. Bur. Stand. Circular* 539, vol. 6, p. 32.
- WINCHELL (A. N.), 1931. *The Microscopic Characters of Artificial Inorganic Solid Substances*. John Wiley, New York.
- 1933. *Elements of Optical Mineralogy*, Part II, Descriptions of Minerals, 3rd edn. John Wiley, New York.
- and WINCHELL (H.), 1951. *Elements of Optical Mineralogy*, Part II. Descriptions of Minerals, 4th edn. John Wiley, New York.

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