20. *Multiple Diffraction in Orthopyroxenes*

Reexaminations of the Space Group

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Thompson (1970),[1] Papike *et al.* (1973)[2] and Matsumoto (1974)[3] have theoretically derived possible space groups of orthopyroxenes with symmetry lower than *Pbca*, which has hitherto been reported to this mineral species. On the other hand, extra reflections that apparently violate the systematic absences characteristic of *Pbca* were observed on the orthopyroxenes from lunar troctolitic granulites (Smyth, 1974)[4] and terrestrial samples (Yamaguchi and Tomita, 1974;[5] Sasaki and Matsumoto, 1974[6]). The present paper, however, is to show that extra reflections from six orthopyroxenes we have so far observed are not structural but merely due to multiple diffraction[7)-9)] from the *Pbca* lattice.

The six samples we used include: enstatite ($En_{93}Fs_7$) in an Alpine-type intrusive harzburgite from Mt. Higashi-Akaishi, bronzite ($En_{90}Fs_{10}$) in a lherzolite included in alkali-olivine basalt from Ichinome-gata, two hypersthenes ($En_{66}Fs_{34}$, $En_{53}Fs_{47}$) in granulites from Ongul-Island and Lützow-Holm Bay in the Antarctica, and enstatite and hypersthene in andesites. The first four samples show reflections in question and the last two samples also show a few of such reflections. Except for those from volcanic rocks the samples are spatially homogeneous within the analytical accuracy of the micro-probe analysis, and no exsolution patterns have been recognized on X-ray single crystal photographs exposed for several days. The minor element contents of these pyroxenes are $Al_2O_3=0.7$–3.9, $CaO=0.1$–0.8, $MnO=0.1$–0.3 and $TiO_2=0$–0.4 in weight per cent.

These orthopyroxenes exhibit weak reflections apparently violating the glide-planes criterion and screw-axes criterion. About twenty weak reflections of the type $hk0$ with $h=2n+1$, several of $0kl$ with $k=2n+1$ and a few of $h0l$ with $l=2n+1$ appear, when X-ray films are exposed for about 200–400 hours. A few reflections of $h=2n+1$, $k=2n+1$ and $l=2n+1$ also appear on $h00$, $0k0$ and $00l$, respectively.

In order to decide whether these reflections are the spots multi-

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ply diffracted or not, firstly long exposure X-ray photographs were taken changing experimental conditions as follows: (1) the direction of incident beam in Weissenberg methods ($\mu=0°$, $3°$, $8°$, $12°$ and $17°$), (2) the values of μ-angle in Buerger precession methods ($\mu=17°$, $20°$, $25°$ and $30°$) and (3) X-ray wave-length (Cu $K\alpha$, Fe $K\alpha$ and Mo $K\alpha$). The ω-2θ technique was used for the same reflections on a four-circle automated diffractometer, Philips PW1100, using Mo $K\alpha$ and Cu $K\alpha$ radiations. The data by four-circle diffractometer are especially useful to examine the $h00$, $0k0$ and $00l$ reflections.

After eliminating the spots obviously due to multiple diffraction revealed by the above procedures, there still remained some forbidden reflections like 1 10 0, 350, 9 10 0, 13 5 0 and 13 6 0. In addition, there were further group of very weak reflections, not consistent with *Pbca*, which were unexceptionally observed in photographs but their relative intensities were unlike the above group of reflections variable from one photograph to another: the reflections include 360, 510, 11 6 0, 19 5 0, 031, 051, 071, 032, 033, 11 0 1, 21 0 0, 050 and 005.

These reflections were then studied in detail using the ψ-scanning method[10] on the four-circle automated diffractometer, which allows rotation of a crystal around reciprocal lattice vectors. The reflections incompatible with *Pbca* symmetry were all examined by the following procedures: (1) each was ψ-step-scanned, at an azimuthal interval of $0.04°$, within the range of $\pm 2°$ from $\psi=0°$ of the bisecting setting, (2) at each step of ψ-azimuth, the integrated intensity with the background corrections was measured by ω-2θ scannings. Then we observed, as shown in Fig. 1, sharp reflections with azimuthal width of around $0.5°$, in most cases of the ψ-step-scannings; they are obviously 'Umweganregung' reflections. In other cases, we observed only zero intensities in the scanning ranges. Thus, all the reflections that apparently violate the space group extinction are caused by multiple diffraction.

In Fig. 2, we give several results of the scannings, each of which was obtained through a complete range of azimuthal angles of $180°$, showing that a number of multiple diffraction peaks occur for each case. Note that in each diagram the entire set of peaks consists of subsets which are symmetrically related to each other about angles separated with an interval of $90°$. Fig. 3a shows the same scanning pattern for 10 0 0 reflection of hypersthene from Ongul-Island, in which the multiple diffraction spectra are overlapped on intrinsic 10 0 0 intensity. In Fig. 3b, it is shown that a change of the integrated intensity on the 231 reflection is partly due to sharp

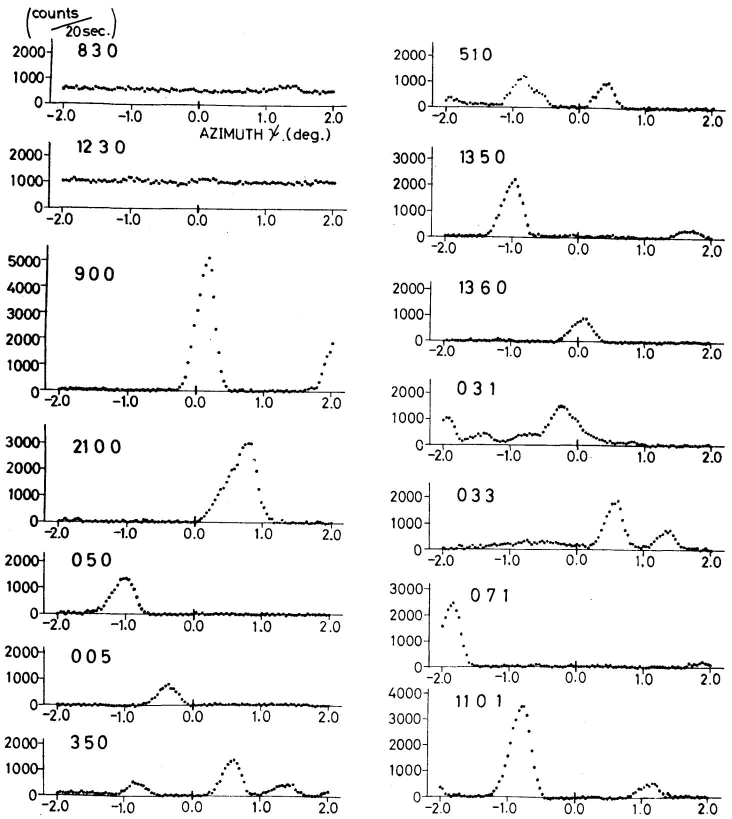

Fig. 1. A spherical crystal, hypersthene from Ongul-Island, is scanned with the following conditions; ω-2θ scans for each ψ-setting, background measurement at each side of the scan, Mo $K\alpha$ (40 KV, 20 mA), graphite monochromator, scan speed (0.04 ω-deg./sec), scan width (0.8 ω-deg.). Umweganregung peaks are observed near $\psi=0°$. Each solid point represents the integrated intensity after background corrections. In X-ray photographs, the 830 and 12 3 0 reflections have weaker intensity than several or many of the reflections apparently violating the space group extinction.

spectra by multiple diffraction, but major swelling is due to anisotropic extinction effect.[11),12)]

The crystal structure of hypersthene from Ongul-Island has been refined, on the basis of the intensity data corrected for directly observed effects on multiple diffraction and anisotropic extinction. Compared to the value of R=0.026 before correcting for these effects, we have obtained, after correction, a significant improved value of R=0.017.

Thus, we may conclude: All the orthopyroxene crystals we have so far examined exhibit no reflections violating the extinction rule

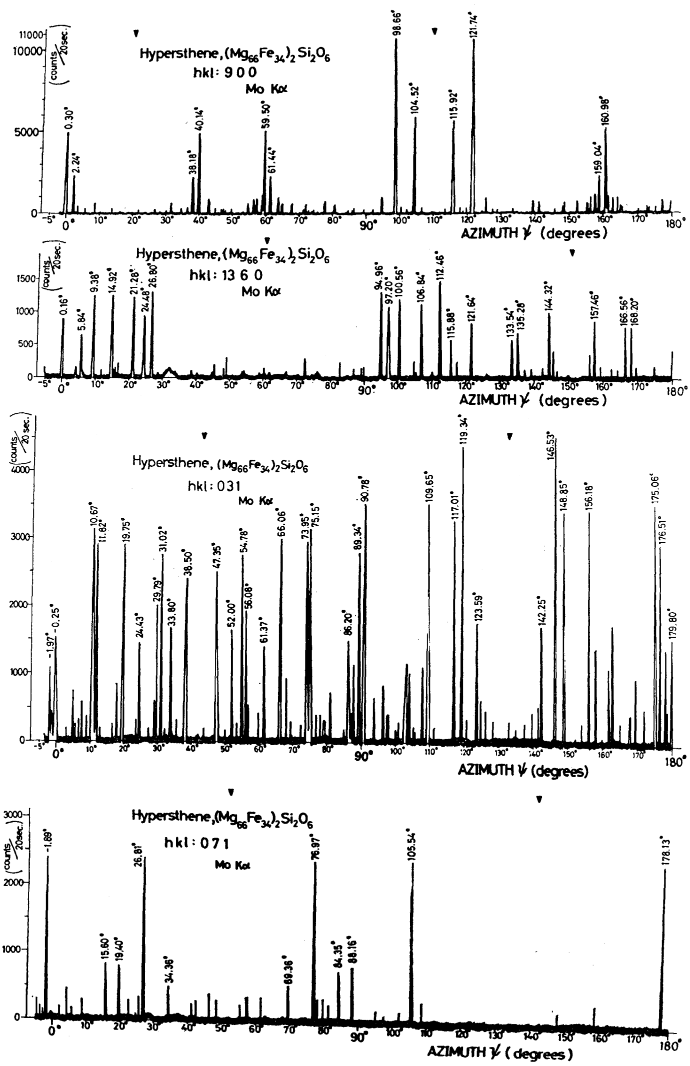

Fig. 2. The 900, 13 6 0, 031 and 071 reflections are step-scanned in ψ-azimuth from −2.0 to 180.0 degrees at intervals of 0.04 degrees. The true intensity is corresponded with the background level. Near the position of symmetrical setting, these reflections have also strong spectra. These spectra can be turned down at intervals of 90 degrees.

for the space group of *Pbca*. The existence of extra reflections that assume lower symmetry is, beyond doubt, due to multiple diffraction. Our study has thus brought out that the occurence of multiple diffraction is surprisingly common in orthopyroxenes. Once extra reflections are observed, due examination should therefore be required before deciding that they are structural.

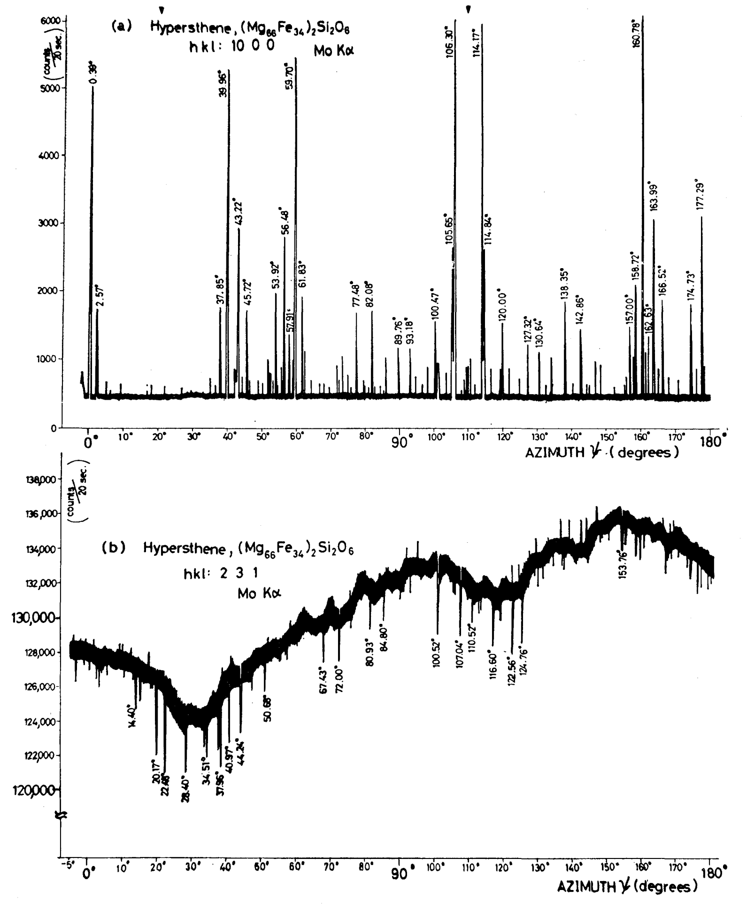

Fig. 3. (a) The Umweganregung peaks appear in intrinsic 10 0 0 intensity. The true intensity is background level with about 500 counts per 20 seconds. (b) Integrated intensities undergoing multiple diffractions (Umweganregung and Aufhellung) and anisotropic extinction (wave-swelling absorption) for the 231 reflection are shown.

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References

1) Thompson, J. B. (1970): Amer. Mineral., **55**, 292.
2) Papike, J. J., Prewitt, C. T., Sueno, S., and Cameron, M. (1973): Z. Krist., **138**, 254.

3) Matsumoto, T. (1974): Miner. Journ., **7**, 4, 374.
4) Smyth, J. R. (1974): Geophys. Res. Let., **1**, 1, 27.
5) Yamaguchi, Y., and Tomita, K. (1974): Mineral. Soc. Japan, 1974 Ann. Meet. Abstr., 23.
6) Sasaki, S., and Matsumoto, T. (1974): Mineral. Soc. Japan, 1974 Ann. Meet. Abstr., 26.
7) Renninger, M. (1937): Z. Phys., **106**, 141.
8) Zachariasen, W. H. (1965): Acta Cryst., **A27**, 119.
9) Isherwood, J., and Wallace, C. A. (1971): Acta Cryst., **A27**, 119.
10) Busing, W. R., and Levy, H. A. (1967): Acta Cryst., **22**, 457.
11) Coppens, P., and Hamilton, W. C. (1970): Acta Cryst., **A26**, 71.
12) Thornley, F. R., and Nelmes, R. J. (1974): Acta Cryst., **A30**, 748.