Supplement

Parameters contained in the model function in RIETAN-2000

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A function to model the calculated intensity, $f_i(\boldsymbol{x})$, is required in Rietveld analysis. It contains peak-shift, background, profile-shape, preferred-orientation, lattice, and crystal-structure, and magnetic-structure parameters. This supplement lists all of these parameters, $\boldsymbol{x}$, to calculate the model function.

A refinement identifier, ID(I), for a parameter A(I) in a group of parameters $\boldsymbol{x}$, specifies the behavior of A(I) during refinement as follows:

ID(I) = 0: Fixed.
       = 1: Refined.
       = 2: Calculated from other refinable parameters using a linear equality constraint.
       = 3: Applied only to primary profile parameters (PPPs) for 'relaxed' reflections (NPRFN = 1–3). A(I) is calculated from secondary profile!parameters (SPPs) in each cycle, which leads to variation of A(I) during the refinement. See Sect. B for details.

A. Global parameters

Table 1 gives parameters independent of phases contained in a sample. Absolute parameter numbers, I, are used for these parameters in RIETAN-2000. They are stored in array A; for example A(2) is D_s. The total number of the background parameters, NUMBG, is 12.

Surface-roughness parameters and their refinement identifiers are never used in neutron powder diffraction but need to be input as dummies.

Table 1   Global parameters input as the first 20 parameters.

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Constants	I	Parameters
	1	NPRFN = 0: Zero-point shift, Z / degree.
		NPRFN = 1–3: t_0.
	2	NPRFN = 0: Specimen-displacement parameter, D_s / degree.
		NPRFN = 1–3: t_1.
	3	NPRFN = 0: Specimen-transparency parameter, T_s / degree.
		NPRFN = 1–3: t_2.
	4	NPRFN = 0: Null.
		NPRFN = 1–3: t_3.
NROUGH	5	NBEAM = 0 or NSURFR = 0: Null.
		NSURFR = 1: Surface-roughness parameter, q_0.
	6	NBEAM = 0 or NSURFR = 0: Null.
		NSURFR = 1: Surface-roughness parameter, q_1.
	7	NBEAM = 0 or NSURFR = 0: Null.
		NSURFR = 1: Surface-roughness parameter, q_2.
	8	NBEAM = 0 or NSURFR = 0: Null.
		NSURFR = 1: Surface-roughness parameter, q_3.
NBCKGR	9	Background parameter, b_0.
	10	Background parameter, b_1.
	11	Background parameter, b_2.
	12	Background parameter, b_3.
	13	Background parameter, b_4.
	14	Background parameter, b_5.
	15	Background parameter, b_6.
	16	Background parameter, b_7.

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B. Primary profile parameters

Partial profile relaxation can be applied only when NPRFN = 1–3. It is not applicable to the pseudo-Voigt fucntion of Thompson, Cox & Hastings (1987): NPRFN = 0. Tables 2, 3, and 4 give PPPs for relaxed reflections (total number: NRELAX, number of PPPs per reflection: NPRIM = 4 for NPRFN = 1 and 3, and NPRIM = 5 for NPRFN = 2). Absolute parameter numbers, I, are used for these parameters in RIETAN-2000.

Note that PPPs are also refined in individual profile fitting (NMODE = 6). In this case, they are input in the same way as whole-pattern fitting under partial profile relaxation, but structure parameters are not necessary.

Table 2   Primary profile parameters (NPRFN = 1).

Constants	I	Parameters
NPPPX	21	FWHM, H / degree.
	22	Asymmetry parameter, A.
	23	Mixing parameter (lower-angle side), η_L.
	24	Mixing parameter (higher-angle side), η_H.
	25	NMODE = 3: $|F_c|$.
		NMODE = 6: const ∞ $|F_c|$.
	26	NMODE = 6: 2θ (peak position).

Table 3   Primary profile parameters for relaxed reflections (NPRFN = 2).

Constants	I	Parameters
NPPPX	21	FWHM of the Lorentzian component, H_1 / degree.
	22	FWHM of the Gaussian component, H_2 / degree.
	23	Asymmetry parameter, A.
	24	Mixing parameter (lower-angle side), η_L.
	25	Mixing parameter (higher-angle side), η_H.
	26	NMODE = 3: $|F_c|$.

Table 4   Primary profile parameters (NPRFN = 3).

Constants	I	Parameters
NPPPX	21	FWHM, H / degree.
	22	Asymmetry parameter, A.
	23	Decay parameter (lower-angle side), m_L.
	24	Decay parameter (higher-angle side), m_H.
	25	$\text{NMODE} = 3: |F_c|.$
		$\text{NMODE} = 6: \text{const} \propto |F_c|.$
	26	$\text{NMODE} = 6: 2\theta \text{ (peak position)}.$

The above parameters are input repeatedly NRELAX times.

RIETAN-2000 has an original new feature called partial profile relaxation. Its development code is 'Margot' after a novel by Alexandre Dumas. For details in partial profile relaxation, please refer to my home page where a PDF file can be browsed:

     http://homepage.mac.com/fujioizumi/recent_research/Rigaku_J/Rigaku_J.html

In conventional Rietveld analysis, PPPs are calculated from SPPs which are refined by a nonlinear least-squares method. In profile-relaxed Rietveld analysis, PPPs are refined independently when part of reflections exhibit marked anisotropic profile broadening. No assumptions are required on the dependence of the PPP's on d. A label for a group of seven PPPs has a form 'PPPn_$h.k.l$,' where n is the phase number, and h, k, and l are indices of a relaxed reflection broadened anisotropically. For example, if reflection 101 for phase No. 1 is broadened anisotropically, label 'PPP1_1.0.1' is input together with seven PPP's, which are refined quite independently of SPPs for the relevant phase. Needless to say, parts of the PPP's may be refined if necessary. Integrated intensities and peak positions for the user-specified reflections are calculated in the same manner as those for the other reflections.

When dealing with X-ray diffraction data of a noncentrosymmetric compound, RIETAN-2000 usually generates Bijvoat pairs, hkl and $\overline{hkl}$, because anomalous dispersion makes their structure factors slightly different from each other. In such cases, PPP's of $\overline{hkl}$ must be constrained (ID(I) = –1) to be equal to corresponding PPP's of hkl.

An ID(I) value of 2 can also be assigned to any PPP. If an A(I) value of 0.0 is input for a PPP of a relaxed reflection, its initial value is calculated from SPPs relevant to the PPP.! If you want to set a PPP at zero practically, input A(I) which is very near to zero, $e.g.$, 10^{-15}.

C. Phase-dependent parameters

Table 5 lists parameters to be assigned for each phase. In samples containing two or more phases, these parameters are input repeatedly.

Table 5   Parameters assigned to each phase.

Constants	K	Parameters
NSFX	0	Scale factor, s.
	1	NPRFN = 0: Gaussian FWHM parameter, U / (degree)^2.
		NPRFN = 1–3: FWHM parameter, U / (degree)^2.
	2	NPRFN = 0: Gaussian FWHM parameter, V / (degree)^2.
		NPRFN = 1–3: FWHM parameter, V / (degree)^2.
	3	NPRFN = 0: Gaussian FWHM parameter, W / (degree)^2.
		NPRFN = 1–3: FWHM parameter, W / (degree)^2.
	4	NPRFN = 0: Scherrer coefficient for Gaussian broadening, P / (degree)^2.
		NPRFN = 1–3: Null.[a)]
	5	NPRFN = 0: Lorentzian Scherrer broadening, X / degree.
		NPRFN = 1–3: a_0.
	6	NPRFN = 0: Anisotropy coefficient for Scherrer broadening, X_e / degree.
		NPRFN = 1–3: a_1.
	7	NPRFN = 0: Strain broadening, Y / degree.
		NPRFN = 1–3: a_2.
	8	NPRFN = 0: Anisotropy coefficient for strain broadening, Y_e / degree.
		NPRFN = 1–3: Null.[a)]
	9	NPRFN = 0 and NASYM = 0: Source width/detector distance, r_s.
		NPRFN = 0 and NASYM = 1: Asymmetry parameter, A_s / degree.
		NPRFN = 1, 2: η_{L0}.
		NPRFN = 3: m_{L0}.
	10	NPRFN = 0 and NASYM = 0: Detector width/detector distance, r_d.
		NPRFN = 0 and NASYM = 1: Null.[a)]
		NPRFN = 1, 2: η_{L1}.
		NPRFN = 3: m_{L1}.
	11	NPRFN = 0: Null.[a)]

	12	NPRFN = 1, 2: η_{H0}.
		NPRFN = 3: m_{H1}.
		NPRFN = 0: Null.[a)]
		NPRFN = 1 and 2: η_{H1}.
		NPRFN = 3: m_{H2}.
	13	NPRFN = 0: Null.[a)]
		NPRFN = 1–3: Anisotropy coefficient for strain broadening, U_e.
	14	NPRFN = 0: Null.[a)]
		NPRFN = 1–3: Anisotropy coefficient for Scherrer broadening, P_e.
NPO1X	15	NPROR = 0: Null.[a)]
		NPROR = 1, 2: Preferred-orientation parameter, p_1.
		NPROR = 3: Preferred-orientation parameter, r.
NPO2X	16	NPROR = 0, 3: Null.[a)]
		NPROR = 1, 2: p_2 / rad^{-2}.[b)]
NAX	17	Lattice parameter, a / Å.
NBX	18	Lattice parameter, b / Å.
NCX	19	Lattice parameter, c / Å.
NALPX	20	Lattice parameter, α / degree.
NBETX	21	Lattice parameter, β / degree.
NGAMX	22	Lattice parameter, γ / degree.
NOTX	23	Overall isotropic atomic displacement parameter, Q / Å^2.

NG1X	24	Occupation factor, g_j.
	25	Fractional coordinate, x_j.
	26	Fractional coordinate, y_j.
	27	Fractional coordinate, z_j.

	28	Isotropic atomic displacement parameter, B_j / Å^2.
		or Anisotropic atomic displacement parameter, β_{11j}.
	29	Anisotropic atomic displacement parameter, β_{22j}.
	30	Anisotropic atomic displacement parameter, β_{33j}.
	31	Anisotropic atomic displacement parameter, β_{12j}.
	32	Anisotropic atomic displacement parameter, β_{13j}.
	33	Anisotropic atomic displacement parameter, β_{23j}.

| | 34 | Magnetic moment, μ_j / μ_B. |

35	Tetragonal, hexagonal, and rhombohedral: Angle between the spin direction and a particular direction of the crystal, ϕ / degree.

36	Orthorhombic, monoclinic, and triclinic: Angle between the spin direction and the a* axis, ϕ_a / degree.
37	Orthorhombic, monoclinic, and triclinic: Angle between the spin direction and the b* axis, ϕ_b / degree.
38	Orthorhombic, monoclinic, and triclinic: Angle between the spin direction and the c* axis, ϕ_c / degree.

a) Both dummy parameters and refinement identifiers (ID) should be set at zero.

b) A dummy parameter and a refinement identifier (ID) of zero must be input in the case of the March-Dollase function (March, 1932; Dollase, 1986).

Up to the first crystallographic site, an absolute parameter number, I, for array A is obtained by KPHB(L) + K, where L is the phase number, and KPHB(L) is the number for the first parameter of phase L (KPHB(1) depends on the number of relaxed reflections), and K is the relative parameter number for a phase-dependent parameter. For multiphase samples, phase-dependent parameters are repeatedly input in the order of increasing phase number, L. The values of the integer constants (NSFX, NPO1X, *etc.*) in the first column are given in SUBROUTINE SETNUM.

Structure parameters (K = 24–34) are repeatedly entered as many times as the number of atoms in the asymmetric unit; subscript *j* denotes the site number. If an overall isotropic atomic displacement parameter, Q, (K = 23) is used to be given a non-zero value, isotropic/anisotropic atomic displacement parameters are skipped. On the other hand, *Q should be not skipped but given a dummy zero value even if isotropic/anisotropic atomic displacement parameters are assigned for atoms in the asymmetric unit*. When the isotropic atomic displacement parameter is assigned to the *j*th site, anisotropic atomic displacement parameters (K = 29–33) are skipped, and *vice versa*.

The magnetic moment (K = 34) is input for only a magnetic atom in neutron diffraction (Shirane, 1959). Angles between the spin direction and the a, b, and c axes (K = 35–38) are necessary only when analyzing neutron diffraction data of non-cubic compounds showing magnetic scattering resulting from collinear spin arrangements (Shirane, 1959). They are input once **with a label** just after the atomic displacement parameter of the last site.

Collinear magnetic structure factors for monoclinic and triclinic systems were derived by N. Yamada (1995) of the University of Electro-Communications independently of the famous work by Shirane (1959).

When NMODE is set at 4, conventional Le Bail refinement (Le Bail, Duroy & Fourquet, 1988) is applicable only to the first phase whereas conventional Rietveld refinement is applied to the other phases, if any (read Sect. 4 in Notes.pdf). That is, structure parameters (K = 23–34) have to be skipped for the first phases when NMODE = 4.

References

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