Anisotropic Fluctuation of Crystallographic Axes under Three-Dimensionally Constraining Dynamic Magnetic Field

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The magnetic axes of a biaxial microcrystal are oriented three-dimensionally by applying dynamic magnetic fields[1] including frequency-modulated magnetic field.[2] Using this phenomenon, we have prepared a composite in which biaxial microcrystalline powder is three-dimensionally aligned in a polymer matrix. We call this composite Magnetically Oriented Microcrystal Array (MOMA). We have reported that MOMA is useful for X-ray single crystal structure analysis.[3] When we use a MOMA, we need to minimize the orientation fluctuation of microcrystals. In this study, we report the relationship between the orientation fluctuation of the magnetic axes and the experimental parameters defining the three-dimensional constraining field.[4]

Under a three-dimensional constraining field, a biaxial microcrystal with three different magnetic susceptibilities $\chi_1 > \chi_2 > \chi_3$, have the following anisotropic magnetic energy

$$E(\omega) = C_x{\omega_x}^2 + C_y{\omega_y}^2 + C_z{\omega_z}^2, \qquad (1)$$

where ω_x, ω_y, and ω_z are infinitesimal rotational angles around three laboratory axes, *x*, *y*, and *z*, respectively. The coefficients C_x, C_y, and C_z are positive constants that depend on the condition of the applied magnetic field and the anisotropy of magnetic susceptibility. The fluctuation of the reciprocal lattice vectors **G**(*hkl*) is governed by the energy shown in eq. 1. The probability density function that the vector **G** orients to the direction defined by the angles α, and β, which are the longitude and latitude directions of the reciprocal lattice sphere, respectively, is expressed as follows:

$$f(\alpha,\beta) = k_{\alpha\beta}\exp(-E(\alpha,\beta)/k_\mathrm{B}T). \qquad (2)$$

Here, $k_{\alpha\beta}$ is the normalization constant and $E(\alpha,\beta)$ is expressed by

$$E(\alpha,\beta) = a\alpha^2 + b\alpha\beta + c\beta^2 \quad, \qquad (3)$$

where *a*, *b*, and *c* are constants depending on C_x, C_y, C_z, Θ, and Φ. The angles Θ and Φ designate the direction of **G**. In Fig. 1, contour maps for $E(\alpha,\beta) = \mathrm{const.}$ are shown for several representative reciprocal lattice vectors. The inclination of the principle axes is different depending on the direction of the **G** vector characterized by (*hkl*).

To evaluate the theory, the fluctuation of $\mathbf{G}(13\bar{1})$ of an L-alanine MOMA was investigated. An L-alanine microcrystalline powder suspended in UV curable monomer was subjected to intermittent rotation in a static magnetic field, followed by irradiation of UV light to photopolymerize the monomer. The MOMA thus prepared was subjected to X-ray diffraction measurements. Fig. 2 shows the comparison of the experimental and theoretical results obtained for $\mathbf{G}(13\bar{1})$. Agreement in shape is excellent, but the absolute magnitude of the fluctuation was larger than that of theoretical ellipsoid. This could result from the shrinkage of the matrix monomer when it was photopolymerized.

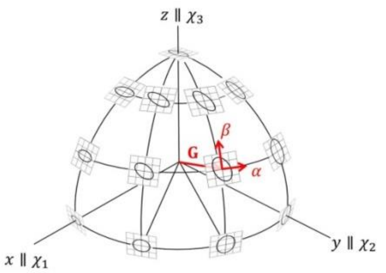

Fig. 1 Contour maps of $\mathrm{E}(\alpha,\beta)$= const. for several reciprocal lattice vectors.

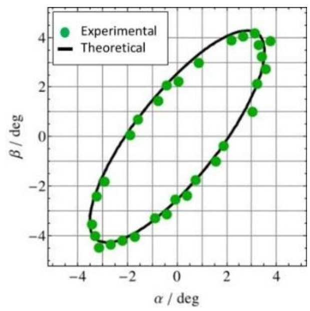

Fig. 2 Contour maps of experimental plots and theoretical ellipsoid of $\mathbf{G}(13\bar{1})$.

References

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