We have investigated the antiferroquadrupolar (AFQ) order in DyB$_2$C$_2$ by resonant x-ray scattering. X-rays with energies near the $L_3$ absorption edge of Dy were employed. Superlattice peaks that correspond to three kinds of propagation vectors of (1 0 0), (1 0 1/2) and (0 0 1/2) were investigated in detail with polarization analyses. The experimental results are analyzed using a formalism on resonant x-ray scattering and a model of the AFQ order. The magnetic and quadrupolar scatterings are explained by the model satisfactorily. A detailed investigation on the critical behavior of the AFQ ordering is also reported. The critical exponent $\beta$ is deduced to be 0.35, not far from the three-dimensional Heisenberg system. We have also succeeded in detecting the diffuse scattering above $T_Q$.
ferromagnetic (AFM) moments in magnetic fields. Since the directions of the induced magnetic moments are coupled with the underlying quadrupolar moments, the quadrupolar order parameter can be estimated from symmetry arguments. However, both the form-factor measurement and the induced-moment measurement require magnetic field, which changes the unperturbed state in zero field.

Appropriate method for each substance and purpose has been employed. In holmium, since it shows ideally the spiral magnetic structure, measurement of higher harmonics is directly connected to the aspherical component. Then the detailed measurement of the temperature dependence of the aspherical component by neutron scattering in zero magnetic field was possible. This is not the case for high symmetry systems like NdMg, CeB₆ and TmTe. We need to rely on x-ray scattering if we want to detect quadrupolar order in zero field, unless the sample exhibits periodic lattice distortion which is detectable with neutrons as in UPd₃Cu₂. A great advantage of the non-resonant x-ray scattering is that we can obtain the absolute value of the ordered quadrupolar moment.

The purpose of the present study is to observe the quadrupolar and magnetic order parameters of a rare-earth compound DyB₂C₂ in zero magnetic field. We have employed the x-ray scattering for this purpose, which has recently been applied to the observations of the orbital orders in 3d transition metal oxides. This method utilizes the characteristic that an atomic scattering factor is largely enhanced when the energy of an x-ray is tuned at an absorption edge of the atom. The first advantage of this method is the high count rate due to the enhancement at the absorption edge. This makes possible to measure temperature, azimuthal angle, polarization, and energy dependences of the peak intensities in detail. Secondly, the element selectivity guarantees the resonant peak arise only from the element in study without doubt. Thirdly, we can distinguish periodic arrangement of the quadrupolar moments from periodic lattice distortions by measuring the energy dependence of the superlattice peak. Finally, the experiment can be performed with a small piece of single crystal using natural boron, which makes neutron scattering experiment difficult. An advantage is firstly that this method is not as direct as the non-resonant x-ray Thomson scattering; it is not possible to deduce the absolute value of the moment. Secondly, the scattering mechanism has not yet been solidly established. Several scattering mechanisms in the orbital ordered state are proposed from different viewpoints, particularly in 3d compounds. In the present study we simply assume that the 5d state is most influenced by the local 4f electrons through the Coulomb and exchange interactions, which we believe is the natural interpretation of the resonance in 4f-electron systems. We will analyze the data quantitatively using the formulations developed by Blume.

DyB₂C₂, with the tetragonal LaB₂C₂-type structure, is a compound that has recently been investigated in detail by Yamauchi et al. and is considered to show an AFQ order. Two phase transitions are clearly observed at 15 K and at 25 K with an entropy release of R ln 2 and R ln 4, respectively. The three phases are named phase I for T > 25 K, phase II for 15 K < T < 25 K, and phase III for T < 15 K. No magnetic order appears in the phase II. The magnetic order in the phase III exhibits an unusual magnetic structure shown in Fig. 1. The structure is represented by the four propagation vectors: k₁ = (1 0 0), k₂ = (1 0 1/2), k₃ = (0 0 0), and k₄ = (0 0 1/2). The basic magnetic structure, where the magnetic moments on a c-plane lie along the [1 1 0] directions with those on the neighboring c-plane along the [1 1 0] directions, is described by k₁ and k₂. Canting of the moments from the [1 1 0] directions by an angle of 28° is described by k₃ and k₄. These properties can naturally be understood by assuming an underlying AFQ order. The propagation vector of the AFQ order that is consistent with the basic magnetic structure is expected to be (0 0 1/2) if we assume a strong spin-orbit coupling.

The first resonant x-ray scattering experiment on DyB₂C₂ was performed by Hirota et al. They discovered two kinds of superlattice reflections of k₂ = (1 0 1/2) and k₄ = (0 0 1/2) that appear below TₐQ = 25 K from incident energy, temperature, azimuthal angle, and polarization dependences, they established that these signals arise from the AFQ order. In particular, the characteristic azimuthal-angle dependences for the σ – σ′ (∝sin² 2φ) and the σ – π′ (∝cos² 2φ) scatterings were considered to reflect the AFQ order of the 4f electrons. Another reflection of k₁ = (1 0 0) was also found to appear below Tₐ = 15 K only for the σ – π′ scattering, reflecting the AFM order. Tanaka et al. also performed a similar experiment independently, though without polarization analysis, and obtained consistent experimental results.

This paper deals with more comprehensive data and analysis than the first reports of Refs. and . The experimental results will be connected quantitatively with the physical picture of the AFQ order using the basic formalism described in Sec. Section describes the
II. THEORY

In order to analyze our experimental results we use the formalism based on symmetry arguments developed by Blume. We summarize the equations in this section. Since we deal with the scattering only in the vicinity of the absorptron edge, we do not consider the non-resonant terms. The elastic resonant scattering amplitude including up to electric quadrupole transition can be written as

$$A_t = -\frac{e^2}{m}\frac{m\omega^3 a}{\omega} \sum_{\alpha,\beta} e^{i(\mathbf{k}\cdot\mathbf{r}_a)} e^{i\mathbf{k}^\prime\mathbf{r}_a} e^{i\mathbf{k}\cdot\mathbf{r}_a}$$

$$\times \left\{ \sum_{\gamma,\delta} \left\langle a | R_m^\alpha | c \right\rangle | c | R_m^\beta | a \right\rangle \right\rangle$$

$$\times \left\{ \sum_{\gamma,\delta} \left\langle a | Q_m^{\gamma\delta} | c \right\rangle | c | Q_m^{\gamma\delta} | a \right\rangle \right\rangle$$

where

$$R_m^\alpha = \sum_{i \in m} r_{i\alpha}$$

$$Q_m^{\alpha\beta} = \sum_{i \in m} r_{i\alpha} r_{i\beta}$$

are the electric dipole and quadrupole moment operators. \( \mathbf{k}(\mathbf{k}') \) and \( \mathbf{e}(\mathbf{e}') \) are the wave vector and the polarization vector of the incident(scattered) photon, respectively; \( \alpha, \beta, \gamma, \) and \( \delta \) vary over the cartesian indices \( x, y, \) and \( z. \) The scattering vector is written by \( \mathbf{k} = \mathbf{k} - \mathbf{k}'. \) The initial and intermediate states of the sample with energies \( E_a \) and \( E_c \) are represented by \( |a\rangle \) and \( |c\rangle \), respectively; \( \hbar \omega \) is the energy of the photon and \( \hbar \omega_0 \) is equal to the energy difference \( E_c - E_a. \) \( \mathbf{n} \) represents the position of the \( n \)-th unit cell and \( \mathbf{d}_m \) represents the \( m \)-th atom in the \( n \)-th unit cell with the Debye-Waller factor \( W_m. \) In Eqs. (3) and (8) the summations are taken over all the electrons of the \( m \)-th atom. \( p_a \) is the thermodynamic probability that the sample is in the state \( |a\rangle. \) We have introduced \( \Gamma, \) the width of the resonance, which corresponds to the lifetime of the intermediate state.

The scattering amplitude for the electric dipole (E1) transition is written as

$$A_{E1} = -\frac{e^2}{m\omega^3} \sum_{n,m} e^{i\mathbf{k}\cdot\mathbf{r}_n} e^{i\mathbf{k}\cdot\mathbf{r}_m} f_{n,m}^\alpha$$

$$\times \left\{ \sum_{\alpha,\beta} \left\langle a | R_m^\alpha | c \right\rangle | c | R_m^\beta | a \right\rangle \right\rangle$$

$$\times \left\{ \sum_{\gamma,\delta} \left\langle a | Q_m^{\gamma\delta} | c \right\rangle | c | Q_m^{\gamma\delta} | a \right\rangle \right\rangle$$

where \( f_{n,m}^\alpha \) is the atomic scattering factor tensor for the E1 transition written by

$$f_{n,m}^\alpha = \sum_{a,c} p_a \frac{|a| R_m^\alpha |c\rangle |c| R_m^\beta |a\rangle}{\hbar\omega - \hbar\omega_0 - i\Gamma/2}.$$
\[ K_u = \frac{1}{2} \varepsilon_x k_z \]
\[ K_v = -\frac{1}{2 \sqrt{3}} (\varepsilon_x k_x - \varepsilon_y k_y) \]
\[ K_\xi = \frac{1}{2 \sqrt{3}} (\varepsilon_y k_x + \varepsilon_z k_y) \]
\[ K_\eta = \frac{1}{2 \sqrt{3}} (\varepsilon_z k_x + \varepsilon_y k_y) \]
\[ K_\zeta = \frac{1}{2 \sqrt{3}} (\varepsilon_x k_y + \varepsilon_y k_x) \]  

(10)

When we assume a special axis for the \( m \)-th atom and take this axis as the \( x \)-axis as in the case of E1 transition, the atomic scattering factor for the E2 transition can be written as

\[
g = \begin{pmatrix}
g_{uu} & g_{uv} & 0 & 0 & 0 \\
g_{uv} & g_{vv} & 0 & 0 & 0 \\
0 & 0 & g_{\xi \xi} & 0 & 0 \\
0 & 0 & 0 & g_{\eta \eta} & 0 \\
0 & 0 & 0 & 0 & g_{\zeta \zeta}
\end{pmatrix}
\]  

\[ + \begin{pmatrix}
0 & 0 & \sqrt{3} g_{v \xi} & 0 & 0 \\
0 & 0 & g_{v \xi} & 0 & 0 \\
0 & 0 & 0 & g_{v \eta} & 0 \\
0 & 0 & 0 & 0 & g_{v \zeta}
\end{pmatrix}, \]  

(11)

where

\[ g_{uu} = 12 b_2 + 4 e_2 + e_4 - 8 f_2 \]
\[ g_{uv} = -\sqrt{3} (4 e_2 + e_4 + 4 f_2) \]
\[ g_{vv} = 12 b_2 + 12 c_2 + 3 e_2 \]
\[ g_{\xi \xi} = 12 (b_2 - f_2) \]
\[ g_{\eta \eta} = 12 (b_2 + c_2) \]
\[ g_{\zeta \zeta} = 12 (b_2 + c_2) \]  

(12)

and

\[ g_{v \xi} = -12 a_1 \]
\[ g_{v \eta} = -12 (a_1 + b_1). \]  

(13)

The coefficients \( b_2, e_2, c_2, f_2 \) are for the symmetric part of the scattering factor and \( a_1 \) and \( b_1 \) are for the asymmetric part, respectively. These are the same coefficients used in Ref. 28 and include the same energy dependence as in the E1 transition. The asymmetric part is purely of magnetic origin and the symmetric part contains both magnetic and quadrupolar contributions.

We notice from Eq. (11) that there appears the cross term of dipole and quadrupole transitions. We do not consider this contribution in this paper because the Dy atom is located at the center of symmetry and the cross term vanishes.

The wavevectors and the polarization vectors for the scattering configuration illustrated in Fig. 2 are written as

\[
k = k(0, \cos \theta, -\sin \theta) \\
k' = k(0, \cos \theta, \sin \theta) \\
\varepsilon_x = (1, 0, 0) \\
\varepsilon_y = (0, \sin \theta, \cos \theta) \\
\varepsilon'_x = (1, 0, 0) \\
\varepsilon'_y = (0, -\sin \theta, \cos \theta). \]  

When the sample is rotated around the \( z \)-axis by an azimuthal-angle \( \varphi \), the rotation matrix

\[
U(\varphi) = \begin{pmatrix}
\cos \varphi & \sin \varphi & 0 \\
-\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1
\end{pmatrix}
\]  

(15)

must be operated to all of the vectors in Eq. (14) from the left.

III. EXPERIMENTAL

The crystal was grown by the Czochralski pulling method with a tetra-arc furnace. The obtained single crystal was checked by powder x-ray diffraction, which showed a single phase pattern of DyB2C2. The temperature dependence of the magnetic susceptibility also agreed with the data reported in Ref. 29.

X-ray scattering measurements were performed on a four circle diffractometer at BL-16A2 of the Photon Factory in KEK. A sample with a c-plane surface was analyzed using the PG(0 0 2) fundamental reflection. The contamination of the (0 0 2) fundamental reflection was estimated to be 1.5% from the intensity ratio \( \pi - \pi' / \sigma - \sigma' \) of the (0 0 2) fundamental reflection.

IV. ORDERED STATE

A. experimental results

The investigation of the reflection corresponding to \( k_3 = (0 0 1/2) \) was performed using the (0 0 5/2) reflection. The incident energy dependence of the intensity at
30 K, 20 K and 10 K, which correspond to the phases I, II, and III, respectively, is shown in Fig. 2. The measured peak top intensities have been transformed into the integrated intensities by multiplying the width so as to be compared with other figures in the same scale. To compare the integrated intensities with the calculated intensities, the data have been corrected for the absorption and for the Lorentz factor; the absorption coefficient was deduced from the fluorescence spectrum.

Resonant peaks are clearly observed in the spectra at 10 K and 20 K, while they are not observed at 30 K. The main-edge peak at 7.792 keV corresponds to the resonance due to the $2p \leftrightarrow 5d$ electric dipole transition. The pre-edge peak at 7.782 keV, which is well resolved in the fluorescence spectrum, is probably attributed to the $2p \leftrightarrow 4f$ electric quadrupole transition. These assignments are consistent with the previous experiments on substances including Dy or other rare-earth elements. Concerning the $\sigma - \sigma'$ process it was not possible to decide if there was any resonance at 7.782 keV because of the wide peak at the main-edge. A very small peak was observed at 10 K for the $\sigma - \sigma'$ process at $\varphi = 0^\circ$. This result is rather confusing since the peak is located between 7.792 keV and 7.782 keV.

The temperature dependences of the integrated intensities have been measured for each resonant peak in Fig. 3.b and c), while those which are observed only at 10 K appear below $T_N = 15$ K (Fig. 3a and d)). Then the former peaks can be attributed to quadrupolar origin and the latter to magnetic origin. With regard to the main-edge and pre-edge peaks in Fig. 3 c), the intensities at $\varphi = 0^\circ$ exhibit the same temperature dependence.

Figure 4 shows the azimuthal-angle dependences of the integrated intensity at 7.792 keV. Peak profile was measured by the $\theta - 2\theta$ scan for each point and was fit to a Gaussian. The intensity of the $\sigma - \pi'$ process exhibits $\sin^2 2\varphi$ dependence below $T_Q$. The intensity of the $\sigma - \pi'$ process exhibits $\cos^2 2\varphi$ dependence at temperatures between $T_Q$ and $T_N$, and some magnetic contribution is added below $T_N$. The azimuthal-angle dependence of the pre-edge peak for the $\sigma - \pi'$ process is shown in Fig. 3 c). The intensity exhibits completely the same angle dependence with that of the main-edge, i.e., $\propto \cos^2 2\varphi$. With regard to the $\sigma - \sigma'$ process, the intensity at 7.782 keV also exhibits the same azimuthal-angle dependence with that at 7.792 keV. However, it was not possible to separate the pre-edge component from the tail of the main-edge peak.

The incident energy dependences of the integrated intensity of the (1 0 2) and (1 0 5/2) reflections, which correspond to $k_1$ and $k_2$, respectively, are shown in Fig. 5. The scale of the vertical axis is the same as those of Figs. 2 and 3. The measurement of the temperature dependence of these resonant peaks shows that they appear below $T_N$, indicating magnetic origin. It should be noted that there is a small shoulder at the lower energy side of the main-edge, which is more clearly observed in the (1 0 5/2) reflection. This is considered to be of electric quadrupole transition. With regard to the $\sigma - \sigma'$ process, no signal was observed at (1 0 2). On the other hand, the (1 0 5/2) reflection exhibits non-resonant type energy dependence which appear below $T_Q$. This indicates that a periodic lattice distortion occurs simultaneously with the AFQ ordering. This point will be discussed in Sec. VI.

B. analysis

1. model calculation

Let us analyze the above experimental results using the formalism described in Sec. II. Figure 3 illustrates a model of the AFQ order of the 4f electrons of the Dy ions, which is expected from the magnetic structure in the phase III. We introduce the canting angle $\alpha$ as a parameter. We assume each ion has its own special axis depending on the local quadrupolar or magnetic moment, around which the charge distribution is symmetric. We define the direction of the magnetic moment in the phase III as the $x$-axis. Since the spin-orbit coupling is strong, the $x$-axis and the principal axis of the quadrupolar moment coincides. To calculate the scattering amplitudes $A_{E1}$ and $A_{E2}$ at an azimuthal-angle $\varphi$, it is necessary to rotate the vectors in Eq. (4) so that the $xyz$-axes in Fig. 2 coincide with those in Fig. 3 for each ion, i.e., the rotation of $-\pi/4 + \alpha + \varphi$ for Dy(1), $3\pi/4 - \alpha + \varphi$ for Dy(2), $\pi/4 + \alpha + \varphi$ for Dy(3), and $-3\pi/4 - \alpha + \varphi$ for Dy(4) is performed using Eq. (16).

The resonant scattering cross-section is equal to the square of the scattering amplitude $A_{\sigma}$. The intensities of the (0 0 5/2) resonant scattering for the electric dipole (E1) transition are calculated to be

$$|A^\sigma_{k_1,E1}|^2 \propto |2d_2 \cos 2\alpha \sin 2\varphi|^2,$$  \hspace{1cm} (16)

$$|A^\sigma_{k_2,E1}|^2 \propto |2d_2 \cos 2\alpha \cos 2\varphi \sin \theta + 2\sqrt{2}d_1 \sin \alpha \sin \varphi \cos \theta|^2,$$  \hspace{1cm} (17)

and for the electric quadrupole (E2) transition,

$$|A^\sigma_{k_1,E2}|^2 \propto |2(e_2 + f_2) \cos 2\alpha \sin 2\varphi \sin^2 \theta + 2\sqrt{2}(a_1 + b_1(2\cos 2\alpha \sin 2\varphi + \cos 2\varphi - 2\cos 2\alpha)) \cos \varphi \sin \alpha \sin \theta|^2/16,$$  \hspace{1cm} (18)

$$|A^\sigma_{k_2,E2}|^2 \propto |\frac{1}{2}(4c_2 + e_2 + 4f_2) + (4c_2 + e_2 + 4f_2 + 4c_2 + 4f_2) \cos 2\theta | \cos 2\alpha \cos 2\varphi \sin \theta + (\text{terms of } a_1 \text{ and } b_1)|^2/16.$$  \hspace{1cm} (19)

Secondly, the intensities of the (1 0 2) resonant scattering at $\varphi = 0^\circ$ for the E1 transition are calculated to be
The azimuthal-angle dependences of the (0 0 5/2) reflection at 7.792 keV in Fig. 4 are well reproduced by Eqs. (19) and (20). The sin²θ dependence of the σ − σ′ process and the cos²θ dependence of the σ − π′ process are explained by the d₂ term. Between T_N and T_Q, d₁ vanishes and d₂ arises only from the quadrupolar moment of the 4f-electrons. The intensity ratio \(I_{\sigma-\pi'}/I_{\sigma-\sigma'} \approx 0.3\) can be explained by \(\sin^2 \theta = 0.3155\) for the Bragg angle of the (0 0 5/2) reflection. The d₁ term contributes below \(T_N\). If we assume \(\alpha = 28^\circ\) as determined in Ref. [23], we obtain \(d_1 = (f_{yz} - f_{zy})/2i = 0.91\) and \(d_2 = (f_{xx} - f_{yy}) = 2.6\) to explain quantitatively the integrated intensities of the (0 0 5/2) reflection at 10 K by Eqs. (19) and (20). By comparing the integrated intensity with that of the (0 0 2) fundamental reflection (2×10²), which is ascribed to the Thomson scattering of \(4\times88\) electrons, we can deduce that the value of \(d_2 = 2.6\) corresponds to 1.4 electrons (per four molecules).

Below \(T_N\) the ordered magnetic moment also contributes to \(d_2\) through an exchange splitting and a spin polarization of the 5d level. This should manifest below \(T_N\) in the temperature dependence of the intensity. However, the intensity for the σ − σ’ process at \(\varphi = 45^\circ\) does not show any clear kink in the temperature dependence around \(T_N\). This result indicates that \(d_2\) is caused mostly by the quadrupolar moment through Coulomb interaction between 4f and 5d electrons. The contribution of the magnetic moment, which is estimated to be 7.1 \(\mu_B\) in Ref. [29], seems much smaller than that of the quadrupolar moment.

Using Eqs. (21) and (22), the above parameters at 10 K, i.e., \(\alpha = 28^\circ\), \(d_1 = 0.91\), and \(d_2 = 2.6\), give the integrated intensities of 0.11 for the (1 0 2) reflection and 4.17 for the (1 0 5/2) reflection, respectively. The value of 0.11 for the (1 0 2) reflection does not reproduce the experimental result of about 1.5 in Fig. 4. This can be ascribed to the experimental difficulty of rotating the crystal to different reciprocal lattice points without changing the effective volume which contributes to the scattering. However, the calculation at least explains these two magnetic peaks qualitatively.

According to Eq. (17) the intensity of the (0 0 5/2) reflection for the \(\sigma - \pi'\) process at \(\varphi = 45^\circ\) is proportional to \(|d_1 \sin \alpha|^2\). The fact that a finite intensity is observed at 10 K indicates that the canting angle of the magnetic moment is certainly not zero below \(T_N\). On the other hand, Eq. (21) shows that the intensity of the (1 0 5/2) reflection for the \(\sigma - \pi'\) scattering at \(\varphi = 0^\circ\) is proportional to \(|d_2 \sin 2\alpha|^2\) above \(T_N\) since the \(d_1\) term vanishes. The experimental result in Fig. 4 shows that the intensity completely disappears at 20 K. This indicates that the canting angle of the quadrupolar moment could be zero at 20 K since \(d_2\) is definitely not zero at this temperature. Then, it is suggested that the canting of the moments occurs only below \(T_N\).

From Eq. (24) we see that the \(\sigma - \sigma'\) scattering of the (1 0 5/2) reflection can also be a measure of the canting angle. However, since this scattering shows a non-resonant type energy dependence as a result of a periodic lattice distortion, it was difficult to extract the resonant contribution at 7.792 keV with sufficient accuracy to examine the behavior of the canting angle in detail.

### 3. Quadrupole transition

The calculated results are qualitatively consistent with the experimental results. The azimuthal-angle dependence of the (0 0 5/2) reflection for the \(\sigma - \pi'\) process at 7.782 keV shown in Fig. 4 is well reproduced by the quadrupolar terms of \(4e_2 + e_2 + 4f_2 = -g_{uv}/\sqrt{3}\) and \(4(c_2 + f_2) = -(g_{xx} - g_{yy})/3\) in Eq. (19). The quadrupolar term of Eq. (19) is also consistent with the experiment. The very small intensities in Fig. 4(a) and (d) might be the magnetic signal from \(a_1\) and \(b_1\) terms.

The magnitudes of \(g_{uv}\) and \(g_{xx} - g_{yy}\) could be estimated by comparing the intensity of the \(\sigma - \pi'\) process with that of the \(\sigma - \sigma'\) process. However, we were not able to estimate the pre-edge peak intensity for the \(\sigma - \sigma'\)
process because of the difficulty in resolving the resonant peak into two peaks of E1 and E2 transitions.

With regard to the $\sigma - \pi'$ scattering of the (1 0 2) and (1 0 5/2) reflections, the small shoulders around the pre-edge in Fig. 3 can be ascribed to the magnetic signal due to the $a_1$ and $b_1$ terms in Eqs. (24) and (27), respectively. The quadrupolar terms of $c_2$ and $c_2 + f_2$ have the factor of $\sin 2\alpha$ or $\sin 4\alpha$. Then, the fact that the intensity disappears above $T_N$ is consistent with the argument on the canting angle in the previous subsection.

V. CRITICAL PHENOMENON

Our interest here is to investigate the critical phenomena associated with the AFQ ordering by measuring the peak profiles precisely, especially around the transition temperature $T_Q$. While almost all the orbital orderings in manganese oxides exhibit first-order-like phase transitions, the AFQ ordering in DyB$_2$C$_2$ is considered to be of second order. The information on the critical phenomena may give some insight into the mechanism of the interaction between the quadrupolar moments.

We have utilized a Ge (111) crystal as an analyzer to obtain good resolution to observe diffuse scatterings. The longitudinal (0 0 l) scans for both the (0 0 2) fundamental Bragg peak and the well developed (0 0 5/2) superlattice Bragg peak at low temperature were able to be reproduced by a squared Lorentzian with its FWHM 0.0011 Å$^{-1}$. We have therefore assumed this as the resolution function for the present measurement.

We have concentrated in this study on the (0 0 5/2) reflection at $\varphi = 45^\circ$. Although the polarization analysis was not performed, we already know from Fig. 3 that this reflection consists only of the $\sigma - \sigma'$ scattering above $T_N$. The measurement was performed much more precisely than the one in Ref. 30. Although the temperature stability of the thermometer was kept within ±0.01 K, heating of the sample by the beam caused a serious problem in the measurement of the temperature dependence of the weak signals at the critical region. The problem is that the beam intensity changes with the ring current, which decreases typically from 400 mA to 250 mA in a day. This leads to different heating powers. It reached about 0.25 K at most when the beam intensity was high. Therefore, very careful data taking and treatment of the data, namely shifting of the temperature, were necessary.

The integrated intensities and the peak widths were obtained by fitting the profiles to a squared Lorentzian. Figure 3 shows the obtained temperature dependence of the integrated intensity of the (0 0 5/2) reflection for the longitudinal (0 0 1) scans. Note that the scale of the vertical axis is different from the other figures. The intensities below $T_Q$ were fitted to a power law $I \propto ((T_Q - T)/T_Q)^{2\beta}$ with varying the fitting range from 15 K to 25 K. The obtained parameters are $T_Q = 25.52 \pm 0.009$ K and $\beta = 0.35 \pm 0.01$, which are demonstrated by the solid line in the figure. This $\beta$ is different from the previously reported value of 0.18 in Ref. 30; this is probably because the previous measurement did not have enough accuracy to determine the critical exponent due to small number of data points.

The inset in Fig. 3 shows the integrated intensity around $T_Q$. Although a careful data treatment was necessary to estimate the reliable temperatures as described above, it is certain that the intensity does not vanish even above $T_Q$. Increase in the peak width was also observed around $T_Q$. The FWHM of the original profile was deconvoluted with the resolution function and was converted to the inverse correlation length along the c-axis. The result is shown in Fig. 3. Although $\kappa_c$ increases with increasing the temperature above $T_Q$, it was not possible to deduce the critical exponent from these small number of points.

VI. DISCUSSIONS

A. four propagation vectors

We can interpret the appearance of the four propagation vectors in the following way. At $T_Q = 25$ K the AFQ order with $k_4 = (0 0 1/2)$ occurs. The AFQ moment is the principal order parameter and induces the periodic lattice distortion with $k_3 = (1 0 1/2)$ through some quadrupole-strain couplings. It should be noted that (1 0 1/2) and (0 0 1/2) are the equivalent reciprocal lattice points. The resonance can occur also at (1 0 5/2) simultaneously with the resonance at (0 0 1/2). However, we could not identify the resonance at (1 0 5/2) because the non-resonant scattering was dominant in the $\sigma - \sigma'$ process or because the canting angle of the quadrupolar moment could be zero in the phase II.

Below $T_N = 15$ K the AFM order with $k_1 = (1 0 0)$ occurs. The AFM moment becomes the additional order parameter in this phase. Since (1 0 0) and (0 0 0) are the equivalent reciprocal lattice points, the magnetic Bragg peak also appears at $k_3 = (0 0 0)$. Furthermore, since there is already an AFQ order which confines the direction of the magnetic moments, the resultant magnetic structure also gives magnetic Bragg peaks at (1 0 1/2) and at (0 0 1/2). Thus, the four propagation vectors are coupled with each other.

B. periodic displacement of atoms

The non-resonant scattering of the (1 0 1/2) reflection that appears below $T_Q$ indicates a periodic displacement of the atoms, which leads to the Bragg reflection due to the Thomson scattering. Tanaka et al. interpreted this reflection as a displacement of B and C atoms which reduces the symmetry to the space group $P4_2/mnm$.11
Lovesey and Knight recently gave a theoretical calculation [3] in which they explained the (0 0 1/2) resonant peak from the same standpoint as in Ref. [2]. However, we consider that the displacement of B and C atoms is not realistic because the estimated scattering factors of the possible reflections from such structure are not consistent with the experimental results. If we assume the z parameter of the 8j site of \( P4_2/mnm \), where the B and C atoms are located, shifted from the original value of 0.5 to 0.45, the squared structure factor for the (0 0 5/2) reflection becomes only 0.0376 whereas those for (1 1 3/2) and (2 2 3/2) becomes 154.6 and 170.6, respectively. Therefore, much stronger reflections are expected for the two points. However, none of these reflections have been observed. Furthermore, neutron powder-diffraction experiments also do not show any evidence of the displacement of B and C atoms [4].

Since the atomic scattering factor of a Dy ion is much larger than that of B and C, it is natural to attribute the non-resonant (0 0 1/2) reflection to a periodic displacement of the Dy ions. We propose a model, where the Dy(1) and Dy(4) in Fig. 7 are displaced by +\( \delta \) along the c-axis and the Dy(2) and Dy(3) by -\( \delta \). This gives the superlattice reflection at (1 0 1/2). The structure factor for the (0 0 5/2) reflection is calculated to be \( F = -4i f_{Dy} \sin 5\pi \delta /c \), while that for the (0 0 2) fundamental reflection is \( 8 f_B + 8 f_C + 4 f_{Dy} \cos 4\pi \delta /c \). From the observed intensity ratio between (1 0 5/2) and (0 0 2), a reasonable value of \( \delta /c \approx 4 \times 10^{-4} \) is deduced.

We consider this displacement to be related with the characteristic crystal structure, where the Dy ions are located between the hard B-C layers. This displacement corresponds to one of the 30 phonon modes of DyB\(_2\)C\(_2\) at \( k = (0 0 1/2) \). Though there are many other phonon modes that involve displacements of B and C, including the one proposed in Ref. [2], their energy must be very high because they have to modify the strong covalent bonding among the B-C network. On the contrary, the energy scale of the motion of the Dy ions is expected to be small. Then, the position of the Dy ions is considered to be susceptible to quadrupolar orderings through a coupling with the lattice.

There is another reason that the resonant scattering in DyB\(_2\)C\(_2\) reflects the AFQ order itself but not the symmetry of the crystal. The local symmetries of Dy(1) and Dy(2), as numbered in Fig. 7, are different even in the original crystal structure above \( T_Q \). This can give the (1 0 0) resonant scattering even above \( T_Q \), which is not observed experimentally. Then, even though there was any displacement of B and C atoms, the effect on the resonant scattering would be negligible. In addition, the displacement of the Dy ions as we propose is mere \( 4 \times 10^{-4} \), also negligibly small to give any effect on the resonant scattering. Finally, it should be noted that the theory in Ref. [2] can also be applied to our model of the AFQ order without the displacement of B and C but with the same space group \( P4_2/mnm \); since the theory is based only on the local symmetry of Dy, it is not restricted by the mechanism of the symmetry lowering.

### C. critical phenomenon

It has been clarified from the present experiment that the order parameter vanishes continuously through \( T_Q \) and that there is still nonvanishing intensity even above \( T_Q \). The temperature dependence of the order parameter below \( T_Q \) well follows a normal power law with a critical exponent \( \beta = 0.35 \pm 0.01 \), which is not an anomalous value when compared with the 3D-Heisenberg model (0.365) [4] 3D-XY model (0.345) [4] and actual magnetic systems such as EuO (0.36) [4] and MnF\(_2\) (0.31) [4]. These results indicate that the AFQ ordering in DyB\(_2\)C\(_2\) is really a second-order phase transition. Note that we assume in this paper that the intensity of the resonant scattering is proportional to the square of the order parameter. Ishihara and Maekawa discuss this relation in Ref. [2].

Concerning the diffuse scattering, it was very difficult to measure precisely the broadening of the width with increasing temperature due to the weak intensity in comparison with the background. However, it should be noted that this result does not directly mean the absence of diffuse scattering. The present situation seems very similar to the case of critical magnetic scattering in MnF\(_2\) studied by x-ray scattering [4]. It was also not possible to measure diffuse scattering above \( T_N = 67.4 \) K due to weak count rates. However, the diffuse scattering certainly exists and were measured up to 10 K above \( T_N \) by neutron scattering [4]. The width of the neutron scattering profile was ten times larger than that of the x-ray scattering [4].

This problem might be related with the so called two length scales problem. There are some systems in which peak profiles of diffuse scatterings above transition temperatures consist of a narrow central peak and a broad one. Detailed studies on this problem using both neutrons and x-rays showed that x-ray signals are dominated by narrow components because of its small resolution volume, while broad component manifests in neutron scattering [4]. Though the origin of the narrow component has not yet been established, it is interpreted as the near surface effect that is more sensitive for x-rays [4].

The observed inverse correlation length \( \kappa_c \) of DyB\(_2\)C\(_2\) above \( T_Q \) is about \( 5 \times 10^{-4} \) Å\(^{-1} \) at a reduced temperature \( (T - T_Q)/T_Q = 4 \times 10^{-3} \), which is read from Fig. 7. This value is as large as that of the narrow component of holmium measured by resonant x-ray scattering at the same reduced temperature \( (T - T_N)/T_N \). Furthermore, in holmium, broad diffuse scattering with its width ten times wider than the narrow component of x-ray is certainly observed by neutron scattering [4]. Therefore, we should not conclude that there is no broad diffuse scattering in DyB\(_2\)C\(_2\) only from the present x-ray scattering study.
VII. CONCLUSIONS

We have performed the resonant x-ray scattering on DyB$_2$C$_2$ and have investigated the signals that correspond to the AFQ and AFM orders. The experimental results are analyzed both quantitatively and qualitatively using a theory of resonant x-ray scattering and a model of the AFQ order. An important result is that the quadrupolar order parameter manifests especially in the $\sigma - \sigma'$ scattering which little contains the magnetic contribution. We analyzed the resonant peak at (0 0 1/2) which corresponds to the AFQ order using a parameter $d_2 = (f_{xx} - f_{yy})$ in this paper.

The (1 0 1/2) reflection is also an important peak for more detailed study of the AFQ order in this compound. One reason is that the non-resonant $\sigma - \sigma'$ scattering suggests a periodic displacement of the Dy ions below $T_Q$, which is probably caused by a quadrupole-strain coupling that is peculiar in this compound. Another reason is that a detailed investigation of the resonant peak could reveal the behavior of the canting angle of the moments especially in the phase II, i.e., if it is zero or not. Both of these subjects require further studies.

We have also studied the critical phenomenon of the AFQ ordering. The order parameter well follows a normal power law with a reasonable critical exponent for a 3D system. The second-order nature of the phase transition was confirmed from the continuous decrease of the order parameter and the diffuse scattering above $T_Q$.

Finally, although the intra-atomic $d - f$ Coulomb interaction is expected to be the most probable origin of the anisotropic tensor of x-ray susceptibility in the 4f-electron systems, we need further investigation, both theoretically and experimentally, to clarify the mechanism of the scattering process.

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FIG. 1. (left) Crystal structure of DyB2C2 (P4/mbm, a=5.341 Å, c=3.547 Å at 30 K). The magnetic structure is indicated by the arrows. (right) The h-l plane of the reciprocal space. Black marks are the reflection points that were actually investigated in the present experiment.

FIG. 2. The definition of the vectors associated with the x-rays and the axes attached to the crystal.

FIG. 3. Incident energy dependences of the integrated intensity of the (0 0 5/2) reflections corrected for the absorption and the Lorentz factor: (a) $\sigma - \sigma'$ scattering at $\varphi = 0^\circ$, (b) $\sigma - \sigma'$ scattering at $\varphi = 45^\circ$, (c) $\sigma - \pi'$ scattering at $\varphi = 0^\circ$, and (d) $\sigma - \pi'$ scattering at $\varphi = 45^\circ$. Note that the integrated intensity of the (0 0 2) fundamental peak is $2\times 10^5$.

FIG. 4. Azimuthal-angle dependences of the integrated intensity of the (0 0 5/2) reflection for the $\sigma - \sigma'$ and the $\sigma - \pi'$ scatterings at the main-edge. Solid lines are the fits with $\sin^2 2\varphi$ for $\sigma - \sigma'$ and with $\cos^2 2\varphi$ for $\sigma - \pi'$.

FIG. 5. Azimuthal-angle dependence of the integrated intensity of the (0 0 5/2) reflection for the $\sigma - \pi'$ scattering at the pre-edge. Solid line is a fit with $\cos^2 2\varphi$.

FIG. 6. Incident energy dependences of the integrated intensity for the $\sigma - \pi'$ scatterings at $\varphi = 0^\circ$ corrected for the absorption and the Lorentz factor: (a) (1 0 2) reflection and (b) (1 0 5/2) reflection.

FIG. 7. A model of the antiferroquadrupolar order in DyB2C2. The shadows represent the anisotropic charge distributions. The unit cell is expressed by $a \times a \times 2c$, which contains four Dy ions. The canting angle $\alpha$ from the [1 1 0]-equivalent axes is treated as a parameter. The direction of the magnetic moment in the phase III is taken as the x-axis.

FIG. 8. Temperature dependence of the integrated intensity of the (0 0 5/2) reflection for the (0 0 l)-scan at $\varphi = 45^\circ$ measured with a Ge(111) analyser. Solid line is a fit to a power law $I \propto ((T_Q - T)/T_Q)^{2\nu}$. Inset shows the integrated intensity around the transition temperature.

FIG. 9. Temperature dependence of the inverse correlation length along the c-axis obtained by deconvoluting the peak widths to the resolution width. Solid line is a calculated curve for the critical exponent $\nu = 0.7$. Inset shows the peak profile at $T = 25.6$ K. Solid line is a fit to a squared Lorentzian and dotted line is a squared Lorentzian with the same height and with the resolution width.
Integrated Intensity [arb.units] vs Temperature [K]

Parameter Values:
- \( \phi = 45^\circ \)
- \( \beta = 0.35\pm0.01 \)
- \( T_0 = 25.52\pm0.009 \) K

Fig. 8  T. Matsumura et al.

Intensity [cps] vs Temperature [K]

Parameter Values:
- \( \phi = 45^\circ \)
- \( T_0 = 25.52\pm0.009 \) K
- \( \beta = 0.35\pm0.01 \)

Fig. 9  T. Matsumura et al.