Resonant x-ray scattering (RXS) has been utilized extensively as a powerful tool to investigate periodic alignments of local anisotropies caused by, for example, chemical bondings and magnetic orderings \cite{1,2}. Element and electronic-shell selectivity provides valuable information on the anisotropy of a specific ion in solids. When the energy of an incident photon is tuned to an absorption edge of the element in study, a core electron is promoted into one of the unoccupied shells to form an intermediate state. When it decays back to the initial state, a secondary photon is emitted. The cross-section of this resonant process carries information on the anisotropy of the unoccupied shell. Since it was found in manganese oxides that RXS can also be a powerful tool to study orderings of electronic orbitals \cite{3}, the method has also been applied to antiferroquadrupolar (AFQ) orderings in \textit{f} electron systems; e.g., in DyB$_2$C$_2$ and in CeB$_6$ \cite{4,5}.

Observations of the orbital orderings in Mn oxides by RXS have been performed to date mainly using the E1 resonance of the K edge, which measures the anisotropy of the 4\textit{p} state. Different theories have been proposed to explain the mechanism of the observation. One theory states that the 4\textit{p} state reflects the anisotropy of the 3\textit{d} state through Coulomb interaction \cite{6}. However, since the orbital orderings in transition-metal oxides generally accompany Jahn-Teller lattice distortions, the 4\textit{p} states are affected also by the displacements of oxygen ions at the octahedral sites. Another theory states that this effect is much stronger than the Coulomb interaction because of the extended wavefunction of the 4\textit{p} state \cite{7}. Since both theories give the same polarization and azimuthal-angle dependences, it has been difficult to distinguish the two interpretations. Recently, it was shown that the latter mechanism is dominant in Mn oxides from the experimental results on thin films \cite{8}. In 4\textit{f} electron systems, on the other hand, the relation among 4\textit{f} orbital (quadrupolar moment), 5\textit{d} orbital, and lattice has not yet been clarified. Three types of interactions should be considered: coupling between 4\textit{f} and 5\textit{d} and lattice, and d-\textit{f} Coulomb interaction. In the present paper we focus on the RXS from AFQ order in DyB$_2$C$_2$. A theoretical estimation of the RXS intensity claims that the effect of the lattice distortion of B and C atoms on the 5\textit{d} state is much larger than the d-\textit{f} Coulomb interaction \cite{9}.

In DyB$_2$C$_2$ the AFQ order takes place at $T_Q = 24.7$ K, followed by an antiferromagnetic (AFM) order at $T_N = 15.3$ K \cite{10}. The magnetic structure below $T_N$ determined in Ref. \cite{10} is illustrated in Fig. 1. The moments lie in the basal $c$ plane and those at the corner site and the face center site are coupled antiferromagnetically but canted from the ${\langle 1 1 0 \rangle}$ directions. The adjacent moments along the $c$ axis are almost perpendicular with each other. This structure is characterized by four \textit{q}-vectors: $q_1=(1 0 0)$, $q_2=(1 0 0.5)$, $q_3=(0 0 0)$, and $q_4=(0 0 0.5)$. This unusual magnetic structure can be understood only by considering the underlying AFQ order, which is illustrated by the ellipses in Fig. 1.

RXS experiments on DyB$_2$C$_2$ to observe the AFQ order was first performed by Hirota \textit{et al.} and by Tanaka \textit{et al.} using the $L_{11}$ edge of Dy \cite{4}. Later, we made a detailed analysis on the observed resonant reflections using a theory developed by Blume \cite{11}. The calculated scattering amplitudes for each \textit{q}-vector, polarization channel ($\sigma-\sigma'$ or $\sigma-\pi'$), and transition process (E1 or E2) assuming the AFQ and AFM structures shown in Fig. 1 are mostly consistent with the experimental results. In short, the AFQ order is observed at $q_4$ and $q_2$, and a staggered lattice distortion at $q_2$.

However, in the previous works of RXS in DyB$_2$C$_2$, the (0 0 half-integer) reflections for the $\sigma-\sigma'$ channel in the E2 process are hidden in the tail of the E1 reso-
nance, while those for the σ-π’ channel are well resolved. Since the calculated structure factors for the two channels have the same order of magnitudes, the disappearance of the E2 resonance in σ-σ’ has been a mystery. Recently, Tanaka et al. made a systematic RXS study of the (0 0 half-integer) reflections and analyzed the data using the structure factor of the atomic tensors. They ascribed the disappearance to the idea that the rank 2 (quadrupole) and rank 4 (hexadecapole) tensors cancel out in the structure factor of the σ-σ’ channel.

In the present paper, we report our new results of the RXS for the (0 0 2.5) and (3 0 1.5) channels. Solid lines are fits with the structure factor of the atomic tensors, using the structure factor of the atomic tensors. They

Figure 2 shows the energy dependences of the intensity of the (0 0 2.5) reflection in the AFQ phase for the σ-σ’ channel at Ψ = 45° and σ-π’ channel at Ψ = 0°. The data are corrected for the absorption. Solid lines are the fits considering the interference between E1 and E2 resonances. Dotted and dashed lines are the contributions from E1 and E2 processes, respectively, without the interference.

where |F_{λν}|^2 were compared with the data. The parameters obtained are the followings: F_{σσ’}^{(E2)} = -0.00647, F_{σσ’}^{(E1)} = 0.0396, F_{σσ’}^{(E2)} = 0.00738, F_{σσ’}^{(E1)} = 0.0184, Δ_E2 = 7.782 keV, Δ_E1 = 7.790 keV, Γ_E2 = 2.75 eV, and Γ_E1 = 4.39 eV. The mixing parameter r, introduced in Ref. 12, was fixed at unity, which means that the E1 and E2 resonances interfere coherently. It should be noted that the data can be explained with finite F_{σσ’}^{(E2)} of the same order of magnitude as F_{σσ’}^{(E2)} if the sign of F_{σσ’}^{(E2)} is opposite to that of F_{σσ’}^{(E1)}; this is due to the interference effect.

The calculated structure factors of the even rank atomic tensor for the (0 0 half-integer) reflections, using the formalism in Refs. 13 and 14 are written as

$$F_{σσ’}^{(E1)} = A \sin 2Ψ \sin 2φ(T_2^{(2)})_{5d}/ \sqrt{T_2^{(2)}}_{5d},$$

$$F_{σσ’}^{(E2)} = A \cos 2Ψ \sin θ \sin 2φ(T_2^{(2)})_{5d}/ \sqrt{T_2^{(2)}}_{5d},$$

for the E1 process and

$$F_{σσ’}^{(E1)} = B \sin 2Ψ \sin^2 θ \sin 2φ \sqrt{T_2^{(2)}}_{4f}/ \sqrt{T_2^{(2)}}_{4f},$$

$$F_{σσ’}^{(E2)} = -B \cos 2Ψ \sin θ \sin 2φ \sqrt{T_2^{(2)}}_{4f}/ \sqrt{T_2^{(2)}}_{4f} .$$

for the E2 process, where sin^2 θ = 0.315 for (0 0 2.5). A and B are the positive constant factors in F(E1) and

FIG. 1: Top view of the crystal structure of DyB2C2. Arrows indicate the magnetic moments in the AFM phase. Ellipses indicate the schematic views of pancake-like charge distributions of 4f electrons below T_q. Their flat planes are perpendicular to the magnetic moments. The B-C layers are located at z = 0.5.

FIG. 2: Incident energy dependences of the intensity of the (0 0 2.5) reflection in the AFQ phase for the σ-σ’ channel at Ψ = 45° and σ-π’ channel at Ψ = 0°. The data are corrected for the absorption. Solid lines are the fits considering the interference between E1 and E2 resonances. Dotted and dashed lines are the contributions from E1 and E2 processes, respectively, without the interference.
Note that the $E_1$ and $E_2$ resonances have the same azimuthal-angle dependence for both polarization channels. $\langle T^{(K)}_q \rangle$ represents the matrix element of the $q$th component of the atomic tensor of rank $K$ in the local ionic coordinates, where the principal axis of the quadrupolar moment is taken as the $x$ axis and the $c$ axis of the crystal as the $z$ axis. The $x$ axis coincides with the direction of the magnetic moment in the AFM phase, which is canted from the (1 0 0) directions by an angle $\phi$. Since the ion is in the local symmetry of $2/m$ in the AFQ phase, $\langle T^{(K)}_q \rangle$ with $K$ even has only the components $q = \pm 2$ and the relation $\langle T^{(K)}_2 \rangle = \langle T^{(-K)}_2 \rangle$ holds. Both $\langle T^{(2)}_2 \rangle$ and $\langle T^{(4)}_2 \rangle$ are real and $\langle T^{(2)}_2 \rangle$ represents the $(x^2 - y^2)$-type quadrupole moment and $\langle T^{(4)}_2 \rangle$ represents the $(x^2 - y^2 - \frac{1}{2}(x^2 - y^2)x^2)$-type hexadecapole moment.

It should be noted that $\langle T^{(K)}_q \rangle$ in the structure factors of $E_1$ and $E_2$ processes represent atomic tensors of the 5$d$ and 4$f$ shells, respectively, which is indicated by the suffix.

If the sign of $\langle T^{(2)}_2 \rangle_{5d}$ is opposite to that of $\langle T^{(2)}_2 \rangle_{4f}$, we have opposite signs for $F_{\sigma\sigma'}^E$ and $F_{\sigma\sigma'}^F$ and the same signs for $F_{\sigma\sigma'}^{(E2)}$ and $F_{\sigma\sigma'}^{(E1)}$, $F_{\pi\pi'}^{(E2)}$ and $F_{\pi\pi'}^{(E1)}$ have the same order of magnitudes if we ignore the rank 4 tensors. This is consistent with the fitting result of the data and can explain the obscure and distinct features of the $E_2$ resonance of the $\sigma$-$\sigma'$ and $\sigma$-$\pi'$ channels, respectively. The present analysis can also explain the experimental results in Ref. 12. Indeed, the data for $\sigma$-$\sigma'$ can actually be fitted with vanishing $E_2$ term as claimed in Ref. 12 if we use larger $\Gamma_{E1}$ for $\sigma$-$\sigma'$. However, the rank 4 term in $F^{(E2)}$ is not necessary to explain the result. This is justified by the azimuthal-angle dependence of the $E_2$ resonance for the (3 0 1.5) reflection, where only the feature of the rank 2 tensor is observed with no indication of the rank 4 tensor; this point will be presented in detail in a forthcoming paper.

The above analysis also applies to the RXS of the (3 0 1.5) reflection, where a large nonresonant Thomson scattering from the lattice distortion also interferes. Concerning the lattice distortion below $T_Q$, Adachi et al. recently presented firm evidence that B and C atoms are shifted along the $c$ axis. Here, two cases can be considered. In the first case the BC-1 parallelogram in Fig. 4 is shifted up (down) and the BC-2 is shifted down (up) at $z = 0.5$ (1.5), and in the second case vice versa. The structure factor $F_{\text{lat}}$ for the two cases are the same in magnitude but opposite in sign. Although the sign cannot be determined by normal Thomson scattering, analysis of the interference with the resonance makes it possible as described next.

Figure 3 shows the incident energy dependence of the intensity of the (3 0 1.5) reflection. The nonresonant region far below the absorption edge do not exhibit azimuthal-angle dependence, while the intensities at energies of $E_1$ and $E_2$ resonances vary with the azimuthal angle, indicating that there are indeed resonances.

We have calculated the structure factors of the rank 2 atomic tensor for the (3 0 1.5) reflection and have found that the sign of $\langle T^{(2)}_2 \rangle_{5d}$ must be opposite to that of $\langle T^{(2)}_2 \rangle_{4f}$ to explain the result in Fig. 3, which is consistent with the (0 0 2.5) reflection. Further, in order to explain the resonances of $E_2$ and $E_1$ processes in the $\sigma$-$\sigma'$ channel, where the Thomson scattering also interferes, the sign of $F_{\text{lat}}$ must be opposite to that of $\langle T^{(2)}_2 \rangle_{4f}$ because the coefficient of $\langle T^{(2)}_2 \rangle_{4f}$ in $F^{(E2)}$ is negative. This means that the first case of the shift of the B-C parallelogram is realized, and not the second case. A simulation of the interference among nonresonant Thomson scattering, $E_2$ resonance, and $E_1$ resonance is demonstrated in Fig. 4. $F_{\text{calc}}$ represents the coefficient of $\langle T^{(2)}_2 \rangle$ in the calculated structure factors.

It must be noticed that the matrix element of $\langle T^{(2)}_2 \rangle$ involves the reduced matrix element, which contains information of the intermediate state and can be positive or negative depending on the ion species. When the charge distribution of 4$f$ electrons of a Dy ion is extended along the $y$ direction of the local coordinates, the quadrupolar moment $Q_{22} (= J_x^2 - J_y^2)$ is positive. The matrix element $\langle T^{(2)}_2 \rangle_{4f}$ then becomes negative because the reduced matrix element of Dy$^{3+}$ for rank 2 is negative. Non-zero $\langle T^{(2)}_2 \rangle_{5d}$ value is caused by the lifting of the degeneracy of $yz$ and $zx$ type 5$d$ orbitals in the tetragonal environment. The local lattice distortion of B and C atoms in the present case will favor the $yz$ type orbital, which extends along the $y$ direction and has less mixing with the $2p$ orbitals of B and C than the $zx$ type orbital.
However, the calculation of $\langle T_2^{(2)} \rangle_{5d}$ for the $yz$ orbital, following the formalism described in Ref. 13, gives a negative value, whereas $\langle T_2^{(2)} \rangle_{5d}$ becomes positive for the $zx$ orbital. Then, the result of the analysis that the signs of $\langle T_2^{(2)} \rangle_{4f}$ and $\langle T_2^{(2)} \rangle_{5d}$ are opposite indicates that the $zx$ orbital is favored in the $5d$ state.

The present analysis assumes localized atomic states both for $4f$ and $5d$ states with fixed energy levels in the framework of the idealized scattering length. We have also assumed that $F_{\text{lat}}$, $F^{(E2)}$, and $F^{(E1)}$ interfere coherently. Actually, a resonance is composed of many intermediate states with slightly different energies. Although the consistent explanation of the data supports these assumptions, it should be examined by more realistic theoretical calculations that take into account complex energy levels of the intermediate state.

In conclusion, the charge distributions of the $4f$ and $5d$ electrons of Dy are extended along the directions that are orthogonal with each other because of the $d$-$f$ Coulomb interaction. This result is consistent with the recent re-examination of the RXS intensity. The relation with the lattice distortion is such that the B-C atoms in the direction where the $4f$ charge distribution is extended move away from Dy, while those in the direction where the $5d$ charge distribution is extended move close to Dy. Although the $5d$ orbital seems to be strongly coupled with the lattice, the present result indicates that the $4f$ orbital is much more strongly coupled with the lattice. The resultant lattice distortion is such that the quadrupole-strain interaction of the $4f$ electrons gains energy, overwhelming the coupling between $5d$ and the lattice. This may be because the $yz$ and $zx$ orbitals in the $5d$ state are almost empty and they have little effect on the total energy when the lattice is distorted. Energy band calculation of LaB$_2$C$_2$ shows that the conduction band of the La $5d$ state consists of the $xy$ orbital. It is expected that a small amount of $zx$ component is induced in the AFQ phase by the $d$-$f$ Coulomb interaction, giving rise to the $E1$ resonance.

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[1] D. H. Templeton and L. K. Templeton, Acta Cryst. A 41, 133 (1985); 41, 365 (1985); 42, 478 (1986); V. E. Dmitrienko, ibid. 39, 29 (1983).
[2] D. Gibbs et al., Phys. Rev. Lett. 61, 1241 (1988); J. P. Hannon et al., ibid. 61, 1245 (1988); 62, 2644(E) (1989).
[3] Y. Murakami et al., Phys. Rev. Lett. 80, 1932 (1998); Y. Murakami et al., ibid. 81, 582 (1998).
[4] K. Hirota et al., Phys. Rev. Lett. 84, 2706 (2000); Y. Tanaka et al., J. Phys.: Condens. Matter 11, L505 (1999).
[5] H. Nakao et al., J. Phys. Soc. Jpn. 70, 1857 (2001); F. Yakhou et al., Phys. Lett. A 285, 191 (2001).
[6] S. Ishihara and S. Maekawa, Phys. Rev. Lett. 80, 3799 (1998); Phys. Rev. B 58, 13442 (1998).
[7] I. S. Elfimov, V. I. Anisimov, and G. A. Sawatzky, Phys. Rev. Lett. 82, 4264 (1999); M. Benfatto, Y. Joly, and C. R. Natoli, ibid. 83, 636 (1999); P. Mahadevan, K. Terakura, and D. D. Sarma, ibid. 87, 066404 (2001); M. Takahashi, J. Ishigishi, and P. Fulde, J. Phys. Soc. Jpn. 68, 2530 (1999).
[8] H. Ohsumi et al., J. Phys. Soc. Jpn. 72, 1006 (2003); T. Kiyama et al., J. Phys. Soc. Jpn. 72, 785 (2003); Y. Wakabayashi et al., Phys. Rev. B 69, 144414 (2004).
[9] J. Igarashi and T. Nagao, J. Phys. Soc. Jpn. 72, 1279 (2003).
[10] H. Yamauchi et al., J. Phys. Soc. Jpn. 68, 2057 (1999).
[11] T. Matsumura et al., Phys. Rev. B 65, 094420 (2002).
[12] Y. Tanaka et al., Phys. Rev. B 69, 024417 (2004).
[13] S. W. Lovesey and E. Balcar, J. Phys.: Condens. Matter 8, 10983 (1996); S. W. Lovesey, ibid. 8, 11009 (1996); S. W. Lovesey and E. Balcar, ibid. 9, 4237 (1997); S. W. Lovesey, O. Fritz, and E. Balcar, ibid. 10, 501 (1998).
[14] S. W. Lovesey and K. S. Knight, Phys. Rev. B 64, 094401 (2001).
[15] H. Adachi et al., Phys. Rev. Lett. 89, 206401 (2002).
[16] T. Nagao and J. Igarashi, Physica B 329-333, 628 (2003).
[17] H. Harima, in Newsletter of Scientific Research on Priority Areas (B) "Orbital Orderings and Fluctuations", Vol. 2, No. 2, p. 24, 2001 (unpublished).