Direct Observation of Antiferroquadrupolar Ordering: Resonant X-Ray Scattering Study of DyB_2C_2

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Antiferroquadrupolar (AFQ) ordering has been conjectured in several rare-earth compounds to explain their anomalous magnetic properties. No direct evidence for AFQ ordering, however, has been reported. Using the resonant x-ray scattering technique near the Dy L_{III} absorption edge, we have succeeded in observing the AFQ order parameter in DyB_2C_2 and analyzing the energy and polarization dependence. The much weaker coupling between the orbital degrees of freedom and the lattice in $4f$ electron systems than in $3d$ compounds makes them an ideal platform to study orbital interactions originating from electronic mechanisms.

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Magnetic ions in a highly symmetrical crystalline environment may have an orbital degeneracy in the crystal electric field (CEF) ground state. With decreasing temperature, this degeneracy is lifted by some interactions. A typical example is the cooperative Jahn-Teller (JT) distortion [1], where the *orbital degrees of freedom,* coupled with a lattice distortion, give rise to a structural phase transition to lower crystalline symmetry. This kind of long range orbital ordering (OO) was confirmed in KCu_2F_4 by polarized neutron scattering [2] and in $LaMnO_3$ by resonant x-ray scattering [3]. Although OO need not be associated with a cooperative JT distortion, as reported in $La_{0.88}Sr_{0.12}MnO_3$ [4], coupling with other degrees of freedom, such as the charge and lattice, is strong in $3d$ compounds [5,6].

In $4f$ electron systems with a degenerate ground state, however, orbital degrees of freedom may remain and undergo a phase transition without a structural distortion, because of the much weaker coupling between the lattice and the well-localized $4f$ orbitals. Such a possibility was first discussed in cubic CeB_6 as a long range ordering of electric quadrupole moments of $4f$ orbitals [7]. Quadrupole ordering is defined as a phenomenon whereby that f electron charge distribution *which diagonalizes certain quadrupole moments* orders spontaneously and spatially as the temperature is lowered. In a ferroquadrupole (FQ) arrangement, aligned quadrupole moments uniformly distort the lattice through a linear coupling between the quadrupole moment O_Γ at the wave vector $q = 0$ and the strain ϵ_Γ of the same symmetry. Therefore, the order parameter can be obtained by measuring a JT-like lattice distortion [8]. In an antiferroquadrupole (AFQ) arrangement, however, the AFQ order parameter is at $q \neq 0$ and does not linearly couple with the uniform strain. Thus, an atomic displacement is not always expected, making it extremely difficult to observe the order parameter.

In this Letter, we present the first direct evidence for AFQ ordering with a resonant x-ray scattering study of DyB_2C_2 near the Dy L_{III} absorption edge. As shown in Fig. 1, DyB_2C_2 has the $P4/mbm$ tetragonal structure consisting of metallic Dy layers and covalently bonded B-C networks stacking alternatively along the c direction [9–11].

Recently, Yamauchi *et al.* [9] reported that DyB_2C_2 exhibits phase transitions at $T_Q \sim 25$ K and $T_N \sim 16$ K. Specific heat measurements showed two distinct λ-type anomalies at T_Q and T_N, each of which releases the entropy equivalent to $R\ln 2$. Since Dy^{3+} ($4f^9$, $^6H_{15/2}$) is a Kramers ion, two Kramers doublets must be involved in these successive transitions. It is thus expected that the ground and first excited Kramers states are close *or* nearly degenerate and that quadrupole degrees of freedom

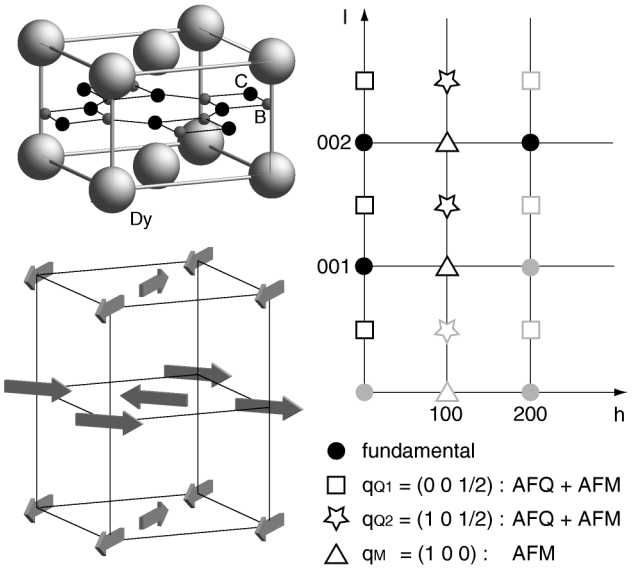

FIG. 1. (Left) Crystal and magnetic structures of DyB_2C_2 ($P4/mbm$: $a = 5.341$ Å, $c = 3.547$ Å at 30 K). (Right) q positions of the fundamental reflections as well as the q_{Q1}, q_{Q2}, and q_M peaks.

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remain. In contrast to the specific heat result, almost no anomaly was observed in the magnetic susceptibility at T_Q and no structural transition nor lattice distortion were confirmed at T_Q and T_N. Thus, the transition at T_Q is neither magnetic nor structural. Neutron diffraction revealed antiferromagnetic (AFM) ordering below T_N. The spins are aligned within the c plane and the magnetic structure is basically described with two propagation vectors $[1\,0\,0]$ and $[0\,1\,\frac{1}{2}]$, indicating that Dy magnetic moments realize 90° arrangement along c, which is hard to be explained from the magnetic interactions alone. They also found weak magnetic signals at $[0\,0\,0]$ and $[0\,0\,\frac{1}{2}]$, indicating that moments are slightly canted within the c plane. From these results, they proposed that the phase I ($T > T_Q$) is paramagnetic, the phase II ($T_N < T < T_Q$) is the AFQ ordered phase, and the phase III ($T < T_N$) is the AFM and AFQ ordered phase.

We have grown a DyB_2C_2 single crystal by the Czochralski method. The crystal was checked by powder x-ray diffraction, which shows a diffraction pattern consistent with Ref. [9], with no detectable foreign phases. The temperature dependence of magnetization is also in good agreement with that of Ref. [9]. X-ray scattering measurements were performed on a six-axis diffractometer at the beam line 16A2 of the Photon Factory in KEK. A piece of the sample with the $(0\,0\,1)$ surface ($\sim 2 \times 2 \times 2$ mm^3) was mounted in a closed cycle ^{4}He refrigerator so as to align the c axis parallel to the ϕ axis of the spectrometer. The mosaic was about 0.07° FWHM. The azimuthal angle Ψ (rotation around the scattering vector) is defined to be 0° when the b axis is in the scattering plane. The incident energy was tuned near the Dy L_{III} edge, which was experimentally determined to be 7.792 keV from fluorescence measurement. To separate the linearly polarized σ' ($\perp$ the scattering plane) and π' ($\parallel$ the scattering plane) components of diffracted beam, we used the PG (006) reflection, for which the scattering angle is about 91° at this energy, resulting in almost complete polarization: the σ-π'/σ-σ' intensity ratio at $(0\,0\,2)$ was less than 0.5%. In our configuration, $(0\,0\,2)$ intensity at Dy L_{III} for σ-σ' is $\sim 2.5 \times 10^6$ counts per second (cps) when the ring current is 300 mA.

AFQ ordering may be directly observed by exploiting the sensitivity of x ray scattering to an anisotropic f electron distribution. In the present study, we have utilized the ATS (anisotropic tensor of x-ray susceptibility) technique, which was originally developed for detecting "forbidden reflections" which appear due to the asphericity of atomic electron density [12,13]. The ATS reflections, which are usually very weak, would increase near an absorption edge because the anomalous scattering, sensitive to an anisotropic charge distribution, is dramatically enhanced. This technique has been successfully applied to the study of OO phenomena in the $3d$ oxides [3–6]. We therefore tuned the incident energy of x rays to the Dy L_{III} edge, where $2p_{3/2} \rightarrow 5d_{5/2}$ dipole and $2p_{3/2} \rightarrow 4f_{7/2}$ quadrupole transitions are expected.

To look for the AFQ and AFM order parameters, we made scans along $(0\,0\,l)$, $(\frac{1}{2}\,0\,l)$, $(1\,0\,l)$, $(h\,0\,2)$, $(\frac{1}{2}\,\frac{1}{2}\,l)$, $(1\,1\,l)$, and $(2\,1\,l)$ at Dy L_{III} without polarization analysis. Scans at 30 K showed only fundamental reflections. At 20 K ($< T_Q$), two kinds of superlattice reflections appear; one is characterized by a propagation vector $q_{Q1} = (0\,0\,\frac{1}{2})$ and the other is $q_{Q2} = (1\,0\,\frac{1}{2})$. At 10 K ($< T_N$), additional reflections appear at forbidden reflection for points which the propagation vector is $q_M = (1\,0\,0)$. These temperature dependences suggest that the q_{Q1} and q_{Q2} reflections correspond to the expected AFQ ordering and that the q_M peak results from the AFM order. Figure 1 schematically shows the q positions of the fundamental reflections as well as the q_{Q1}, q_{Q2}, and q_M peaks in the $(h\,0\,l)$ zone.

Figure 2 shows the incident energy dependences of the fluorescence as well as $(0\,0\,2.5)$, $(1\,0\,2.5)$, and $(1\,0\,2)$ reflections, i.e., q_{Q1}, q_{Q2}, and q_M points. The $(0\,0\,2.5)$ peak shows a sharp enhancement at Dy L_{III} in both σ-σ' and σ-π' processes. Note that there exists another

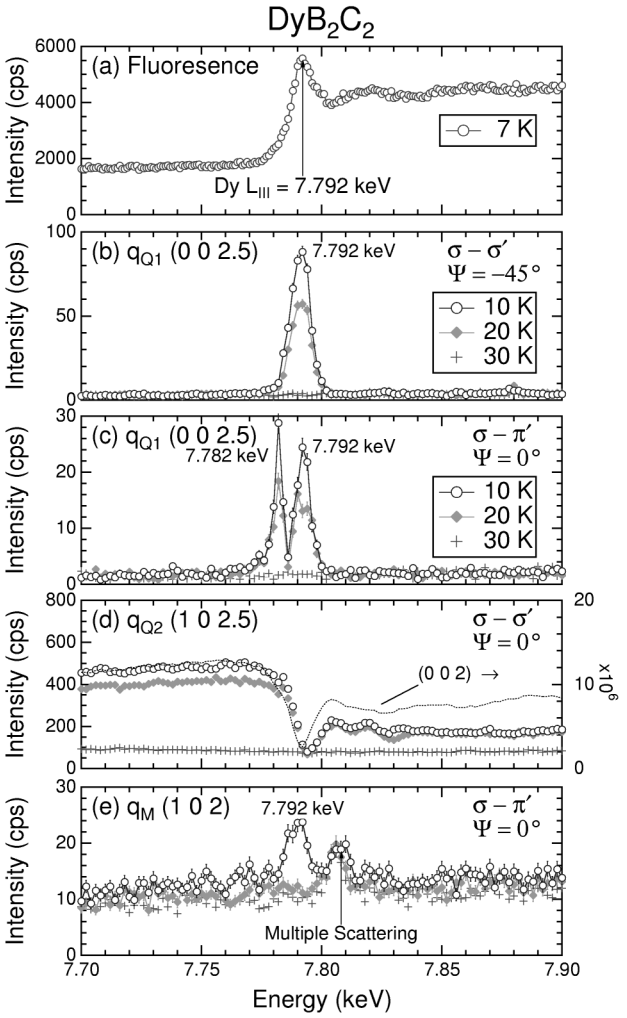

FIG. 2. Incident energy dependences of (a) fluorescence (unpolarized), (b) q_{Q1} peak at $(0\,0\,2.5)$ for σ-σ' polarization, (c) $(0\,0\,2.5)$ for σ-π', (d) q_{Q2} peak at $(1\,0\,2.5)$ for σ-σ', and (e) q_M peak at $(1\,0\,2)$ for σ-π'. No background subtraction was made.

enhancement for σ-π' at 7.782 keV, 10 eV lower than the Dy L_{III} edge, which we speculate corresponds to level splitting within $2p$ and $5d$ states or a quadrupole transition. The (1 0 2) peak shows an enhancement in σ-π' at the Dy L_{III} edge at 10 K. No such enhancement was found in σ-σ' at (1 0 2), indicating that the (1 0 2) reflection is dominated by σ-π' scattering, as expected for dipole resonant magnetic scattering. As for (1 0 2.5), there exists a clear enhancement in σ-π' at Dy L_{III} below T_N indicating a magnetic contribution, which is consistent with Ref. [9]. In contrast, the σ-σ' scattering exhibits *not-enhanced* reflection below T_Q as shown in Fig. 2(d). We first focus upon the resonant peaks, then discuss this *not-enhanced* contribution at (1 0 2.5).

In addition to the enhancement, it is expected that the resonant ATS scattering from AFQ ordering would show an azimuthal angle dependence reflecting the shape of f electron distribution. As shown in Fig. 3, we measured azimuthal dependence for the two different polarizations by rotating the crystal around the scattering vector kept at (0 0 2.5). The (0 0 2.5) intensity has been normalized using the (0 0 2) intensity in the same Ψ to correct for small variations due to extrinsic reasons such as the sample shape. Figure 3 demonstrates that the σ-σ' scattering exhibits a characteristic fourfold oscillation, compatible with the tetragonal symmetry. The intensity approaches zero at $\Psi = 0$ and $\frac{\pi}{2}$. The σ-π' scattering of (0 0 2.5) also shows a fourfold oscillation. However, the oscillation for σ-π' is reversed relative to that of σ-σ'. Plus, the intensity minimum remains finite at 10 K and approaches zero at 20 K, indicating that there exists a magnetic contribution to the σ-π' scattering at (0 0 2.5), which is consistent with Ref. [9]. These azimuthal dependences strongly indicate the existence of anisotropic f electron distribution and the associated AFQ ordering below T_Q.

Figure 4 shows the order parameters measured at (0 0 2.5) and (1 0 2) as well as the spontaneous strain Δc estimated from the (0 0 2) peak position. The order parameters behave as continuous 2nd order transitions and can be fitted to power laws indicated in the figures. The transition temperatures thus obtained are in good agreement with the values reported by Yamauchi *et al.* [9]. The critical exponents β obtained for the AFQ ordering and AFM ordering are about 0.2. The spontaneous strain Δc has the β value close to 0.5, which is twice as much

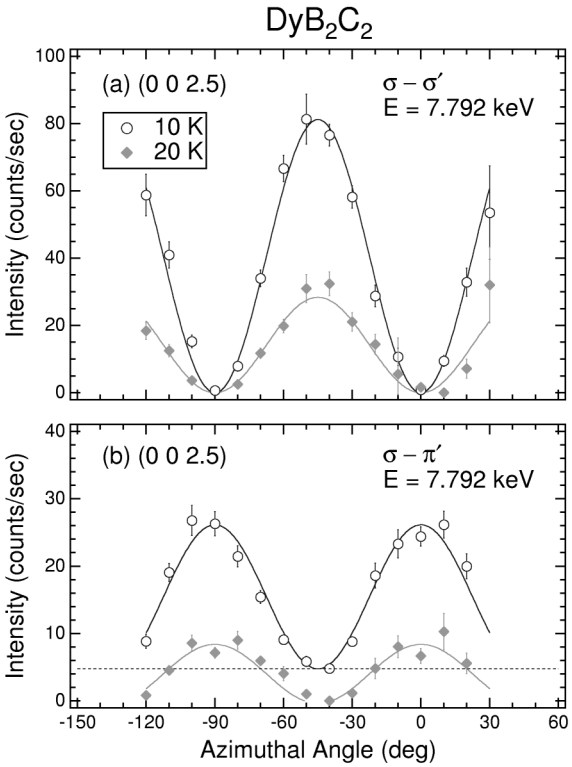

FIG. 3. Azimuthal dependences of a q_{Q1} peak (0 0 2.5) for σ-σ' and σ-π' polarizations. ω-2θ scan was made at each azimuthal angle after lining up the crystal using (0 0 2). Intensity was obtained by fitting a Gaussian to the peak profile. The peak width of (0 0 2.5) shows no particular Ψ dependence and no difference from that of (0 0 2), i.e., the instrumental resolution. The solid curve is proportional to $\sin^2 2\Psi$.

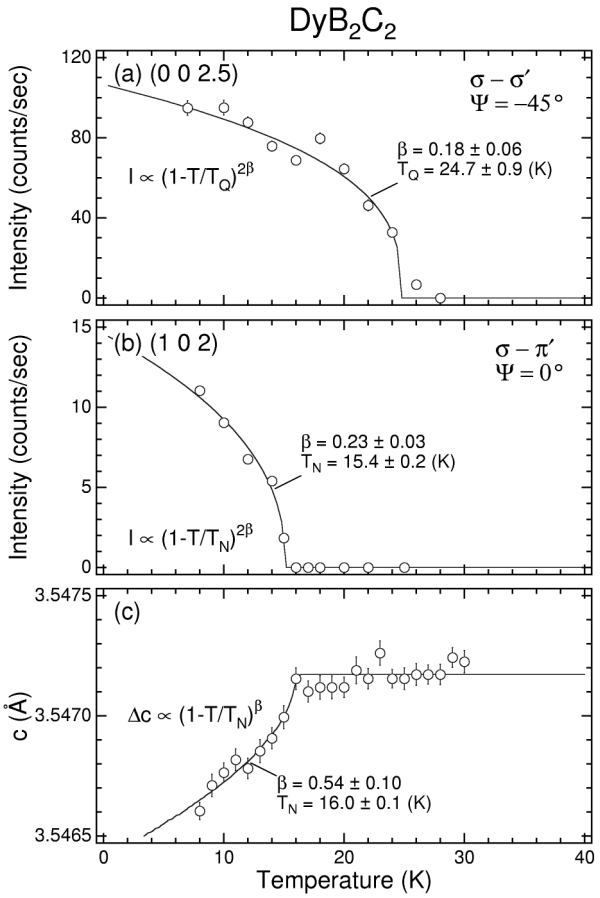

FIG. 4. Temperature dependences of (a) AFQ and (b) AFM order parameters. Peak profiles were obtained at particular polarization and azimuthal conditions so as to maximize the intensities for (0 0 2.5) and (1 0 2), and fitted well to a Gaussian. Peak widths are resolution limited in the temperature range where peaks are visible in our counting statistics (10–15 s per point). (c) Temperature dependence of spontaneous strain Δc estimated using (0 0 2).

as that of the AFM ordering, indicating that Δc is a secondary order parameter and that it is quadratically coupled to the AFM ordering. For quantitative discussions, we need more statistics, which will not only give more precise β values but also provide more information such as correlation lengths above T_N and T_Q.

Note that no anomaly was found in Δc at T_Q, which implies that the quadrupole ordering has only a very weak coupling, if any, to the lattice of DyB_2C_2. Since the superlattice peak at (1 0 2.5) appearing below T_Q is not enhanced and has σ-σ' polarization, similar to fundamental reflections such as (0 0 2), it might be ascribed to atomic displacement. As a simple model for order estimation, let us assume that the Dy ions are displaced along c and that their directions alternate between nearest neighbors. From the intensity ratio below Dy L_{III}, $I(1\,0\,2.5)/I(0\,0\,2) = 4.0 \times 10^{-5}$, we obtain the displacement $\delta = 0.0014$ Å $(0.000\,40c)$. With this small atomic displacement, the change of lattice constant may not be detected by the present x-ray diffraction which resolution is $\Delta c/c \sim 10^{-4}$ [see Fig. 4(c)]. Recently, Benfatto *et al.* [14] theoretically reexamined the resonant x-ray scattering study of $LaMnO_3$ [3] and argued that the resonant signal is mostly due to the JT distortion resulting in anisotropic Mn-O bond lengths. This is in contrast with the theoretical description of Ishihara and Maekawa [15], who proposed a mechanism based upon the Coulomb interaction between $4p$ conduction band and the ordered $3d$ orbitals. In DyB_2C_2, however, it is very unlikely that the lattice distortion results in the observed anisotropic electron distribution. Further study of the (1 0 2.5) reflection is still required, including the azimuthal dependence, and to consider other possibilities such as AFQ ordering.

Let us briefly discuss the CEF of DyB_2C_2. Using the equivalent operator formalism [16,17], we have constructed a point charge model, which shows that the ground ($J_z = \pm\frac{1}{2}$) and first excited ($J_z = \pm\frac{3}{2}$) Kramers doublets almost degenerate and are well separated from the other excited states. These results confirm the existence of a pseudoquartet ground state in which the orbital degrees of freedom remain, and are consistent with a strong planar magnetic anisotropy which aligns the magnetic moments within the c plane [9]. Details of the calculation will be published elsewhere [18].

The present study unambiguously shows that the resonant scattering at q_{Q1} corresponds to the AFQ ordering. However, the mechanism producing such resonant scattering is not completely understood. When allowed, the dipole transition usually overwhelms the quadrupole transition in resonant scattering. Similar to a d orbital angular moment, a quadrupole moment has five elements, i.e., $Q_m^{(2)}$ $(m = 2, 1, 0, -1, -2)$ where $Q_m^{(l)} = \int \rho(\mathbf{r})\mathbf{r}^l \times \sqrt{4\pi/(2l+1)}\, Y_{lm}(\theta, \phi)\, d\mathbf{r}$ in the polar coordinate. In the CEF, the five elements are classified in a particular irreducible representation, which can be conveniently explained by the Stevens's equivalent operators [16]. In the cubic O_h symmetry, for example, they are proportional to $O_2^0 = \{3J_z^2 - J(J+1)\}/\sqrt{3}$ and $O_2^2 = J_x^2 - J_y^2$ in the Γ_3 (e_g) symmetry, and $O_{xy} = J_xJ_y + J_yJ_x$, O_{yz}, and O_{zx} in the Γ_5 (t_{2g}) symmetry. Actual quadrupole moments can be obtained by calculating their expectation values. Through a strong c-f coupling between $5d$ conduction band and localized $4f$ orbitals, the AFQ ordering would be projected onto the $5d$ orbital states. To completely understand the present experimental results, it is necessary to establish much more detailed scattering mechanism in the appropriate CEF symmetry.

In conclusion, the present resonant ATS x-ray scattering study has directly shown the existence of long range AFQ ordering in DyB_2C_2, which had been theoretically conjectured in some f electron systems, and given the order parameter and the information concerning the final polarization and azimuthal dependence, which are directly linked to the type of AFQ moments.

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