Antiferroquadrupolar (AFQ) ordering has been conjectured in several rare-earth compounds to explain their anomalous magnetic properties. No direct evidences for AFQ ordering, however, have 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$_2$C$_2$ and analyzing the energy and polarization dependence. Much weaker coupling between orbital degrees of freedom and lattice in 4f electron systems than in 3d compounds provides an ideal platform to study orbital interactions originated from electronic mechanisms.

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Direct Observation of Antiferro-Quadrupolar Ordering
– Resonant X-ray Scattering Study of DyB$_2$C$_2$ –

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Magnetic ions in a highly symmetrical crystalline may have an orbital degeneracy in the crystalline electric field (CEF) ground state. With decreasing temperature, this degeneracy becomes lifted by some interactions. A typical example is the cooperative Jahn-Teller (JT) distortion, where the orbital degrees of freedom, coupled with lattice distortion, gives rise to a structural phase transition to lower crystalline symmetry. Long range orbital ordering (OO) thus driven was confirmed in KCu$_2$F$_4$ by polarized neutron scattering and in LaMnO$_3$ by resonant x-ray scattering. Although OO is not necessarily associated with the cooperative JT distortion as reported in La$_{0.88}$Sr$_{0.12}$MnO$_3$, coupling with other degrees of freedom such as charge or lattice would remain in 3d compounds.

In 4f electron systems with degenerated ground state, however, orbital degrees of freedom may remain and undergo a phase transition without structural distortion because of much weaker coupling between lattice and well-localized 4f orbitals. Such possibilities was first discussed in cubic CeB$_6$ as long range ordering of electric quadrupole moments of 4f orbitals. Quadrupole ordering is defined as a phenomenon that f electron charge distribution which diagonals certain quadrupole moments orders spontaneously and spatially as lowering temperature. In ferroquadrupole (FQ) arrangement, aligned quadrupole moments uniformly distort the lattice through a linear coupling between quadrupole moment $Q$ at the wave vector $q = 0$ and strain $\epsilon$ in the same symmetry. Therefore, the order parameter can be obtained by measuring JT-like lattice distortion. In antiferroquadrupole (AFQ) arrangement, however, the AFQ order parameter at $q \neq 0$ does not linearly couple with the uniform strain. Thus, atomic displacement is not always expected, which makes it extremely difficult to observe the order parameter.

In this Letter, we present the first direct evidence for AFQ ordering by the resonant x-ray scattering study of DyB$_2$C$_2$ near the Dy $L_{III}$ absorption edge. As shown in Fig. DyB$_2$C$_2$ has the P4/mmb tetragonal structure consisting of Dy layers and B-C networks stacking alternatively along the c direction. Covalently bonded B-C network requires no electron transfer from Dy$^{3+}$ ions (4f$^9$, 6H$_{15/2}$), thus DyB$_2$C$_2$ has three conduction electrons per formula in the 5d band and is metallic.

Recently, Yamauchi et al. reported that DyB$_2$C$_2$ exhibits phase transitions at $T_Q \sim 25$ K and $T_N \sim 16$ K. Specific heat measurement showed two distinct $\lambda$-type anomalies at $T_Q$ and $T_N$, each of which releases the entropy equivalent to $R \ln 2$. Since Dy$^{3+}$ is a Kramers ion, two Kramers doublets should be involved in these successive transitions. It is thus expected that the ground and first excited Kramers states are close or nearly degenerated and that quadrupole degrees of freedom remain.
contrast to the specific heat, 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 \( T_N \). 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 hardly explained only by magnetic interactions. 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\(_2\)C\(_2\) single crystal by the Czochralski method. The crystal was checked by powder x-ray diffraction, which shows a diffraction pattern consistent with Ref. 3 and no detectable foreign phases. The temperature dependence of magnetization is also in good agreement. X-ray scattering measurements were performed on a six-axis diffractometer at the beamline 16A2 of the Photon Factory in KEK. A piece of the sample \((\sim 2 \text{ mm cubic})\) was mounted in a closed cycle \(^4\text{He}\) refrigerator so as to align the \( c \)-axis parallel to the \( \phi \) axis of the spectrometer. The mosaicity was about 0.07° FWHM. The azimuthal angle \( \Psi \) (rotation around the scattering vector) is defined as 0° where the scattering plane contains the \( b \) axis, i.e., \([0 \ 1 \ 0]\). The incident energy was tuned near the Dy \( L_{III} \) edge, which was experimentally determined to be 7.792 keV using fluorescence. To separate the linearly polarized \( \sigma' \) (\( \perp \) the scattering plane) and \( \pi' \) (\( \parallel \) the scattering plane) components of diffracted beam, we used the PG \((006)\) reflection, which scattering angle is about 91° at this energy resulting in almost complete polarization: the \( \sigma - \pi' / \sigma - \sigma' \) intensity ratio at \((0 \ 0 \ 2)\) was less than 0.5 %. In our configuration, \((0 \ 0 \ 2)\) intensity at Dy \( L_{III} \) for \( \sigma - \sigma' \) is \( \sim 2.5 \times 10^6 \) counts per second (cps) when the ring current is 300 mA.

AFQ ordering will 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. 8 9 10 The ATS reflections, which are usually very small, would increase in the resonant x-ray scattering near an absorption edge because the anomalous scattering factor, sensitive to an anisotropic charge distribution, is dramatically enhanced. This technique was successfully applied to the OO phenomena in 3d oxides. 9 11 12 We thus tuned the incident energy of x-rays at Dy \( L_{III} \), where \( 2p_{3/2} \rightarrow 5d_{5/2} \) dipole and \( 2p_{3/2} \rightarrow 4f_{7/2} \) quadrupole transitions are expected.

![Graphical representation](image-url)
\[\sigma - \pi' \\text{ processes. Note that there exists another enhancement for } \sigma - \pi' \text{ at } 7.782 \text{ keV, } 10 \text{ eV lower than the Dy } L_{III} \text{ edge, which we speculate corresponds to level splitting within } 2p \text{ and } 5d \text{ states or a quadrupole transition.} \]

The (1 0 2) peak shows an enhancement in \(\sigma - \pi'\) at the Dy \(L_{III}\) edge at 10 K. No such enhancement was found in \(\sigma - \sigma'\) at (1 0 2), indicating that the (1 0 2) reflection is dominated by \(\sigma - \pi'\) scattering, as expected for resonant magnetic scattering. As for (0 0 2.5), there exists a clear energy enhancement in \(\sigma - \pi'\) at Dy \(L_{III}\) below \(T_N\) indicating magnetic contribution, which is consistent with Ref. [9]. On the contrary, the \(\sigma - \sigma'\) scattering exhibits non-resonant reflection below \(T_Q\) as shown in Fig. 4(d). We first focus upon the resonant peaks, then discuss this non-resonant contribution at (1 0 2.5).

In addition to the enhancement, it is expected that the resonant ATS scattering from AFQ ordering shows the azimuthal angle dependence reflecting the shape of f electron distribution. As shown in Fig. 3, we measured azimuthal dependence for two different polarizations by rotating the crystal around the scattering vector kept at (0 0 2.5). Figure 3 demonstrates that the \(\sigma - \sigma'\) scattering exhibits a characteristic four-fold oscillation, compatible to the tetragonal symmetry. The intensity approaches zero at \(\Psi = 0\) and \(\frac{\pi}{2}\). The \(\sigma - \pi'\) scattering of (0 0 2.5) also shows a four-fold oscillation. However, the oscillation for \(\sigma - \pi'\) is reversed to that of \(\sigma - \sigma'\). Plus, the intensity minimum remains finite at 10 K and approaches zero at 20 K, indicating that there exists a magnetic contribution to the \(\sigma - \pi'\) 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 \(T_Q\).

Figures 3 show the order parameters measured at (0 0 2.5) and (1 0 2) as well as the spontaneous strain \(\Delta c\) 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 \(\beta\) obtained for the AFQ ordering and AFM ordering are about 0.2. The spontaneous strain \(\Delta c\) has the \(\beta\) value close to 0.5, which is twice as much as that of the AFM ordering, indicating that \(\Delta c\) is a secondary order parameter and quadratically coupled to the AFM ordering. For quantitative discussions, we...
need more statistics, which will not only give more precise $\beta$ values but also provide more information such as correlation lengths above $T_N$ and $T_Q$.

Note that no anomaly was found in $\Delta c$ at $T_Q$, which implies that the quadrupole ordering has very weak coupling, if any, to the lattice of DyB$_2$C$_2$. Since the superlattice peak at (1 0 2.5) appearing below $T_Q$ is non-resonant and has $\sigma-\sigma'$ polarization, it might be ascribed to atomic displacement. As a simple model for order estimation, let us assume that Dy ions are displaced along $c$ and that the directions are alternated 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 $\delta = 0.0014 \text{Å} (0.0004 \text{Å})$. 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. 1(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 another theoretical description by Ishihara and Maekawa, [15] who proposed a mechanism based upon the Coulomb interaction between $4p$ conduction band and the ordered $3d$ orbitals. In DyB$_2$C$_2$, however, it is very unlikely that the lattice distortion results in the observed anisotropic electron distribution. It is still required to further study the (1 0 2.5) reflection, including the azimuthal dependence, and to consider other possibilities such as asphericity of atomic electron density due to AFQ ordering.

Let us briefly discuss the CEF of DyB$_2$C$_2$. Using the equivalent operator formalism, [16][17] we have constructed a point charge model, which shows that the ground ($J_z = \pm \frac{3}{2}$) and first excited ($J_z = \pm \frac{1}{2}$) Kramers doublets almost degenerate and are well separated from the other excited states. These results confirm the existence of a pseudo quartet 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. 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 yielding 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 $Q_{m}^{(l)} = \int \rho(r)r^{l}4\pi r^{2}/(2l+1)Y_{lm}(\theta, \phi)dr$ 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 [19]. In the cubic $O_h$ symmetry, for example, they are proportional to $O_{4h}^{2} = (3J_{x}^{2} - J(J + 1))/\sqrt{3}$ and $O_{x}^{2} = J_{x}^{2} - J_{y}^{2}$ in the $\Gamma_3$ ($e_g$) symmetry, and $O_{xy} = J_{x}J_{y} + J_{y}J_{x}$, $O_{yz}$, and $O_{zx}$ in the $\Gamma_5$ ($t_{2g}$) symmetry. Actual quadrupole moments can be obtained by calculating their expected values. Through a strong $c-f$ coupling between 5$d$ conduction band and localized $4f$ orbitals, the AFQ ordering would be projected onto the 5$d$ orbital states. To completely understand the present experimental results, it is necessary to establish much more detailed scattering mechanism in a proper CEF symmetry.

In conclusion, the present resonant ATS x-ray scattering study has directly shown the existence of long range AFQ ordering in DyB$_2$C$_2$, 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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