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LETTER TO THE EDITOR

Evidence of antiferroquadrupolar ordering of DyB₂C₂

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Abstract. The antiferroquadrupolar ordering in DyB₂C₂ has been investigated using the x-ray resonant scattering technique. The dependence of the intensities of two superlattice peaks on temperature, azimuthal angle, and energy of the incident x-rays was measured. The results show that the antiferroquadrupole ordering, which accompanies a structural phase transition, exists below $T_Q = 25$ K. A structural model for the antiferroquadrupole ordering, for which the propagation vectors are (0, 0, 1/2) and (0, 1, 1/2), is presented.

Rare earth and actinide compounds have been investigated for many years in relation to the physical properties of the highly correlated electron system, such as heavy fermion behaviour, magnetic ordering, superconductivity and so on. Some compounds are supposed to have long-range ordering of the electronic multi-polar moment. For example, it was proposed that CeB₆ has an antiferroquadrupolar (AFQ) ordering phase. The ordering pattern of the quadrupolar moment was determined from the analysis of the induced anti-parallel magnetic moment using neutron diffraction under a magnetic field. However, this indirect technique does not unambiguously reveal the AFQ structure, hence the real nature of the quadrupolar ordering is still an open question.

Recently, Murakami *et al* [1, 2] showed that resonant x-ray scattering can measure the orbital orderings of the manganites directly. In their study, some forbidden reflections exhibit an enormous resonance enhancement at the Mn K edge in the quadrupolar ordered phase, in which the Mn 3d orbitals are arranged in an alternating manner. They also showed that the intensity of the reflections has a strong dependence on the azimuthal angle (the rotation of the sample around the scattering vector). These features are due to the anisotropy of the tensor of susceptibility (ATS) scattering [3], and are basically attributed to the anisotropic form factor of the Mn 4p orbital. The mechanism of how the quadrupolar ordering of the 3d orbitals causes the anisotropy of the 4p orbitals has been explained theoretically using a MnO₆ cluster calculation; the aspherical distribution of the 3d electron due to the quadrupolar ordering may split the 4p orbital states via the Coulomb interaction between Mn 4p and 3d electrons and gives rise to the anisotropic form factor of the 4p orbital [4]. Accordingly, one can extract the ordering pattern of the quadrupole moments directly from x-ray ATS scattering experiments. In this letter, we employ this anisotropic resonant scattering technique to study the AFQ ordering of 4f compounds for the first time, and show direct evidence of the AFQ ordering of the 4f compound DyB₂C₂.

Very recently, Yamauchi *et al* [5] carried out specific heat, magnetization, and neutron scattering measurements and proposed that AFQ ordering exists in DyB₂C₂. There are two large anomalies in the temperature dependence of specific heat. The first, at $T_C = 15.3$ K, corresponds to the magnetic phase transition and the other, at $T_Q = 24.7$ K, is suggested to originate from the AFQ ordering transition. This compound has a tetragonal LaB₂C₂-type structure, which belongs to the space group $P4/mbm$ [6], with $a = 5.34$ Å and $c = 3.56$ Å at room temperature. The structure is described as a stacking of two atomic layers along the c -axis with a–Dy–(B, C)–Dy–sequence, where the Dy atom occupies the $2(a)$ site, and the B and C atoms occupy the two $4(h)$ sites. The magnetic structure below T_C has been determined from the neutron powder diffraction experiment and is described by four propagation vectors, $k_1 = (1, 0, 0)$, $k_2 = (0, 1, 1/2)$, $k_3 = (0, 0, 0)$, and $k_4 = (0, 0, 1/2)$ [5]. The Dy magnetic moment of $7.1 \mu_B$, which is confined in the c -plane, has a zigzag structure with an angle of 90° along the c -axis and is canted from the $[110]$ axis by an angle of 28° .

X-ray diffraction experiments were performed at beamline 4C in Photon Factory, KEK. The incident x-rays were monochromatized by a Si(111) double crystal and focused by a bent cylindrical mirror. The incident energy in the vicinity of the Dy L_{III} absorption edge ($E = 7.789$ keV) was used. A single crystal of DyB₂C₂ grown by the Czochralski method using a tri-arc furnace was mounted in a closed-circle ⁴He refrigerator on a six-axis diffractometer, so that the ϕ -axis is perpendicular to the c -plane (cleavage plane) in order to measure the scattering intensity as a function of azimuthal angle around the c -axis. The dimensions of the crystal were about $1 \text{ mm} \times 3 \text{ mm} \times 0.5 \text{ mm}$.

We show the energy dependence of the intensities of two superlattice peaks at $(0, 0, 3/2)$ and $(0, 1, 1/2)$ measured at 17.3 K ($T_C < T < T_Q$). Figure 1(a) shows the energy dependence of the integrated intensity of the $(0, 0, 3/2)$ reflection together with the intensity of the fluorescence yield measured in an off-Bragg condition, and (b) shows the energy dependence of the peak intensity of the superlattice reflection at $(0, 1, 1/2)$ and the 002 Bragg reflection. It is found that the superlattice peak at $(0, 0, 3/2)$ shows huge resonance enhancement in intensity. The integrated intensity has a main peak at $E = 7.79$ keV and a shoulder peak about 8 eV below the main peak in energy. The main peak is located at the energy of the white line of the fluorescence yield and thus can be attributed to the resonance of the dipole transition $2p_{3/2} \rightarrow 5d$. The shoulder peak is probably accompanied by the transition $2p_{3/2} \rightarrow 4f$ [7]. The small intensity far away from the white line is due to the $\lambda/2$ component of the incident x-rays and thus it is found that the $(0, 0, 3/2)$ peak exists intrinsically only at the Dy absorption edge.

The intensity of the ATS scattering from the AFQ ordering shows the azimuthal angle dependence because of the anisotropic feature of the structure factor [8]. Secondly, we show the azimuthal angle dependence of the integrated intensity of the superlattice peak at $(0, 0, 3/2)$ measured at 17.3 K and 7.79 keV in figure 2. The intensity is normalized by the intensity of the 002 reflection to correct the variation of the sample surface shape. The full curve represents the model calculation which we describe later. The intensity oscillates with 90° period and has a minimum at the azimuthal angle $\Psi = 0$, where the a -axis is in the scattering plane.

These two results, the huge resonant enhancement and the azimuthal angle dependence, clearly show that the superlattice peak at $(0, 0, 3/2)$ originates from the ATS scattering. From the analogy of the manganites, it is concluded that the ordering of the quadrupole moment of Dy³⁺ exists at this temperature. To our knowledge, this is the first direct evidence of the AFQ ordering of 4f compounds.

We show in figure 3 the temperature dependence of the integrated intensity of the superlattice peaks at $(0, 0, 3/2)$ and $(0, 1, 1/2)$ measured with incident x-rays of $E = 7.79$ keV. The intensities of the two peaks increase with decreasing temperature below 25 K ($\sim T_Q$). The

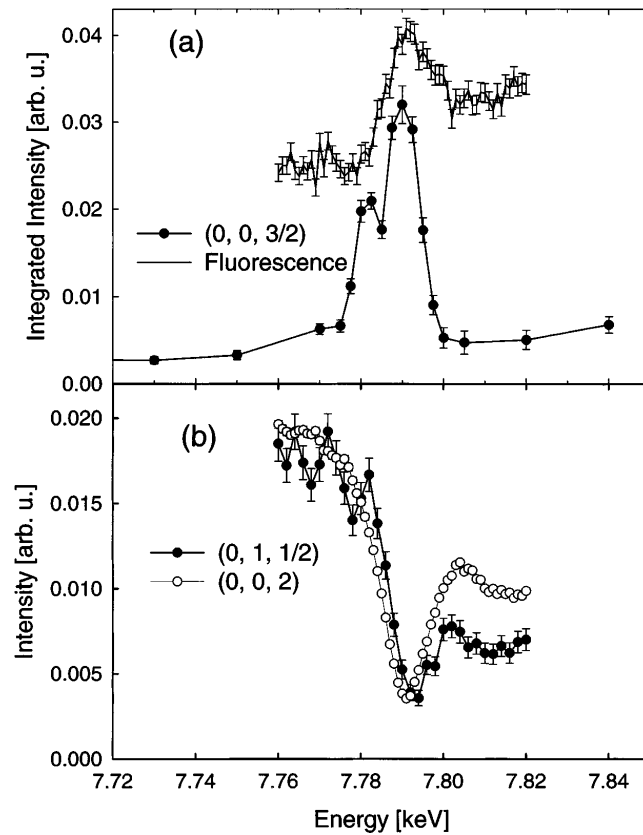


Figure 1. The energy dependence of (a) the integrated intensity of the $(0, 0, 3/2)$ and the intensity of the fluorescence yield measured under an off-Bragg condition at $T = 17.3$ K, and (b) the intensity of the $(1, 0, 1/2)$ peak and that of the $(0, 0, 2)$ peak at $T = 17.3$ K.

intensities above 25 K are attributed to the contribution of the $\lambda/2$ components of the incident x-rays. Thus, the superlattice peaks at $(0, 0, 3/2)$ and $(0, 1, 1/2)$ appear only below T_Q , obviously indicating that the transition at T_Q is due to the AFQ ordering. It seems that the intensity of the $(0, 0, 3/2)$ reflection has a step around 15 K ($\sim T_C$). Further increase below T_C is attributed to magnetic resonant scattering, because in the neutron scattering experiment magnetic Bragg reflections were observed at these positions [5].

In clear contrast to the $(0, 0, 3/2)$ case, the $(0, 1, 1/2)$ peak was observed even in the off-resonant region. As shown in figure 1(b), although small structures around the absorption edge exist, the shape is quite similar to that of the 002 peak, indicating that the energy dependence is mainly caused by the absorption of the Dy^{3+} ion. The intensity of the $(0, 1, 1/2)$ peak, after the absorption correction, is constant over the measured energy range. Hence, the superlattice peak at $(0, 1, 1/2)$ does not come from an anomalous part of the atomic scattering factor but from the usual Thomson scattering. Moreover, as seen in figure 3, the intensity of the $(0, 1, 1/2)$ peak also shows the order parameter of the transition at T_Q . Therefore, the $(0, 1, 1/2)$ peak must stem, mainly, from the lattice distortion accompanied by the AFQ ordering transition.

Important knowledge about the AFQ ordering can be deduced from the superlattice peak due to the lattice distortion as well as the ATS reflection. The above result revealed that the AFQ phase has a lower symmetry than $P4/mbm$. Possible space groups below T_Q are

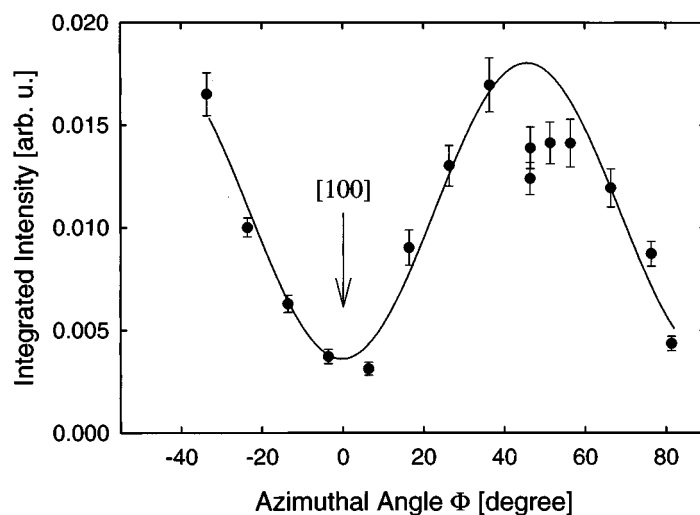


Figure 2. The azimuthal angle dependence of the integrated intensity of the $(0, 0, 3/2)$ reflection. The full curve represents the intensity calculated from equation (1).

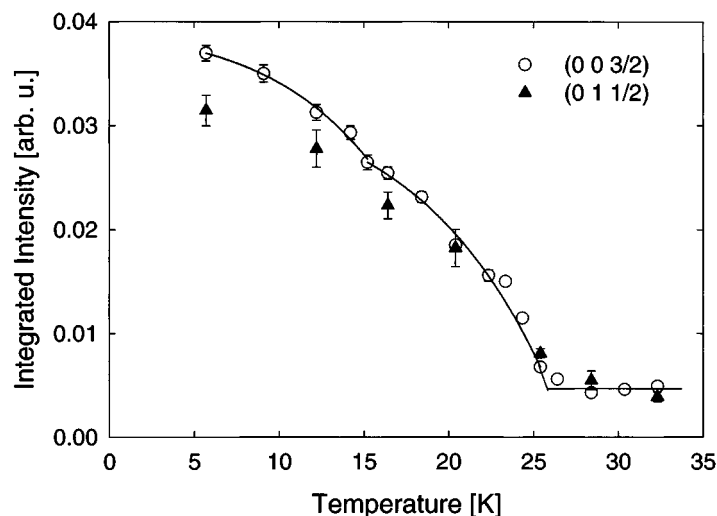


Figure 3. The temperature dependence of the integrated intensity of the peaks of the $(0, 0, 3/2)$ and $(0, 1, 1/2)$ reflections. Lines are drawn only to guide the eye.

$P4/mnc$, $P4_2/mbc$, $P4_2/mnm$, and $P4/mbm$ [9]. Two of them, $P4_2/mbc$ and $P4/mbm$, do not satisfy the observed extinction rule that $(0, 1, 1/2)$ is allowed and $(0, 0, 3/2)$ is forbidden. In addition, there are no plausible atomic positions for $P4/mnc$. Therefore, we conclude that the space group at the AFQ phase is $P4_2/mnm$, where the Dy atom is located at the $4(c)$ site and the B and C atoms are located at the two $8(j)$ sites. We show the structure for DyB_2C_2 in this space group in figure 4 together with a model of the AFQ ordering. The structural phase transition is described by the displacement of the B and C atoms. One pair of the four B (C) atoms in the $z' = 1/4$ plane in the cell of $a \times a \times c'$ ($c' = 2c$) moves upwards slightly and the other pair moves downwards by the same length along the c -axis; the atoms in the

$z' = 3/4$ plane move by the same length in the opposite direction to the transfer direction of the corresponding atoms, which have the same x and y values in the $z' = 1/4$ plane.

We discuss a model of the AFQ ordered phase as follows. According to the local structure around Dy^{3+} , we present the principal axes (x, y, z) of the crystalline field of Dy^{3+} in figure 4. Note that the principal axes of the quadrupole moment are parallel to those of the crystalline field. Thus we propose a model of the AFQ ordered phase where one of the principal axes of the quadrupole moments is arranged as shown by thick lines on Dy atoms in figure 4. Since the principal axes of the quadrupole moment are parallel to those of the crystal field, this is a model of the AFQ ordering which we propose; one of the principal axes of the quadrupole moments orders as shown by thick lines in the AFQ ordered phase. Since the site symmetry of the Dy^{3+} ion changes from $4/m$ to $2/m$, the transition at T_Q is the one which makes the x and y axes inequivalent. The quadrupole moment of the Dy^{3+} ion is expressed by Γ_5 type (O_{xy}, O_{yz}, O_{zx}) and Γ_3 type (O_2^0, O_2^2). In order to determine the type of the quadrupole moment in this compound, further theoretical and experimental investigations should be carried out. Note that the two neighbouring Dy atoms along the c -axis have a zigzag atomic configuration with an angle of 90° . This structure agrees with the magnetic structure proposed from the neutron scattering experiment [5].

In this model, the atomic scattering tensor of the Dy^{3+} is written as

$$\hat{f} = \begin{pmatrix} f_{\parallel} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_c \end{pmatrix}.$$

We denote the sites of the Dy atom at $(0, 0, 0)$, $(1/2, 1/2, 0)$, $(0, 0, 1)$, and $(1/2, 1/2, 1)$ as 1, 2, 3 and 4, respectively. Let the angle between the a -axis and the x -axis of the Dy atom at site 1 be ϕ , then those for the Dy atom at sites 2, 3 and 4 are $90^\circ - \phi$, $90^\circ + \phi$, and $-\phi$, respectively. The tensors at the four sites are obtained as

$$\begin{aligned} \hat{f}_1 &= \begin{pmatrix} f_{\parallel}c^2 + f_{\perp}s^2 & f_{\parallel}cs - f_{\perp}cs & 0 \\ f_{\parallel}cs - f_{\perp}cs & f_{\parallel}s^2 + f_{\perp}c^2 & 0 \\ 0 & 0 & f_c \end{pmatrix} \\ \hat{f}_2 &= \begin{pmatrix} f_{\parallel}s^2 + f_{\perp}c^2 & f_{\parallel}cs - f_{\perp}cs & 0 \\ f_{\parallel}cs - f_{\perp}cs & f_{\parallel}c^2 + f_{\perp}s^2 & 0 \\ 0 & 0 & f_c \end{pmatrix} \\ \hat{f}_3 &= \begin{pmatrix} f_{\parallel}s^2 + f_{\perp}c^2 & -f_{\parallel}cs + f_{\perp}cs & 0 \\ -f_{\parallel}cs + f_{\perp}cs & f_{\parallel}c^2 + f_{\perp}s^2 & 0 \\ 0 & 0 & f_c \end{pmatrix} \end{aligned}$$

and

$$\hat{f}_4 = \begin{pmatrix} f_{\parallel}c^2 + f_{\perp}s^2 & -f_{\parallel}cs + f_{\perp}cs & 0 \\ -f_{\parallel}cs + f_{\perp}cs & f_{\parallel}s^2 + f_{\perp}c^2 & 0 \\ 0 & 0 & f_c \end{pmatrix}$$

where $c = \cos \phi$ and $s = \sin \phi$. The structure factor tensor for $(0, 0, l + 1/2)$, where l is an integer, is given as

$$\hat{f}_1 + \hat{f}_2 - \hat{f}_3 - \hat{f}_4 = \begin{pmatrix} 0 & 4(f_{\parallel} - f_{\perp})cs & 0 \\ 4(f_{\parallel} - f_{\perp})cs & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

According to the calculation of the intensity of the ATS reflection presented by Nagano *et al* [10], the azimuthal-angle dependence of the intensity is given as

$$I(\theta, \Psi) \propto A^2\{(\sin 2\Psi)^2 + (\cos 2\Psi \sin \theta)^2\} \propto \sin^2 2\Psi + \text{constant} \quad (1)$$

where $A = 4(f_{\parallel} - f_{\perp})cs$, Ψ is the azimuthal angle, $\sin \theta \ll 1$, and θ is the Bragg angle for the $(0, 0, 3/2)$ reflection. We show the ATS scattering intensity calculated from equation (1) based on the AFQ structure model in figure 2 (represented by the full curve), which agrees well with the experimental result in terms of not only the period but also the dependence on the orientation.

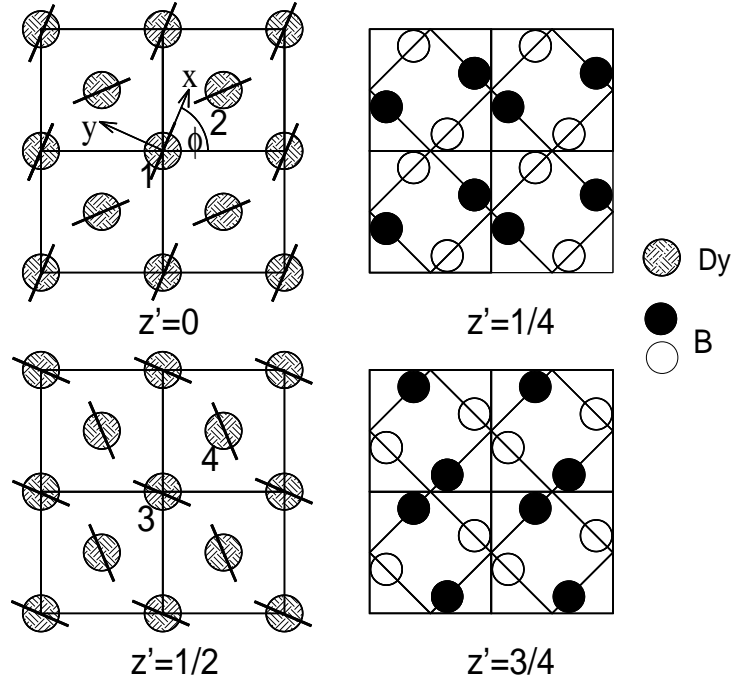


Figure 4. The atomic structure model for DyB_2C_2 in the AFQ phase. Here z' is represented on a scale of $c' = 2c$. Only the B atoms in the plane $z' = 1/4$ and $z' = 3/4$ are shown for convenience. The B atoms at closed circle sites locate slightly downwards along the c -axis, and those at open circle sites locate slightly upwards along the c -axis by the same length. The thick lines on Dy atoms represent one of the principal axes of the quadrupolar moment.

To find out the propagation vectors for the AFQ structure model, we calculated the structure factor tensors. Possible vectors are $(0, 0, 1/2)$, $(0, 1, 1/2)$, $(0, 0, 0)$, and $(1, 0, 0)$. The structure factor tensor for $(0, 0, 1/2)$ is given above. The structure factor tensor for $(0, 1, 1/2)$ is

$$\hat{f}_1 - \hat{f}_2 - \hat{f}_3 + \hat{f}_4 = \begin{pmatrix} 2(f_{\parallel} - f_{\perp})(c^2 - s^2) & 0 & 0 \\ 0 & -2(f_{\parallel} - f_{\perp})(c^2 - s^2) & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

which gives an azimuthal-angle dependence of the intensity as $I(\theta, \Psi) \propto (\cos 2\Psi)^2 + \text{constant}$. Thus, the $(0, 1, 1/2)$ peak has an intensity from the ATS reflection originating from the AFQ ordering as well. The structure factor tensor for $(1, 0, 0)$ is the zero tensor, and that for $(0, 0, 0)$ is given as

$$\begin{pmatrix} 2(f_{\parallel} - f_{\perp}) & 0 & 0 \\ 0 & 2(f_{\parallel} - f_{\perp}) & 0 \\ 0 & 0 & 4f_c \end{pmatrix}$$

which consists of only a symmetric part around the c -axis. Hence, the propagation vectors which represent the AFQ ordering are $(0, 0, 1/2)$ and $(0, 1, 1/2)$.

In summary, the resonant x-ray scattering technique was utilized for the first time for observing the AFQ ordering of 4f compounds. We measured the intensities of the superlattice peaks of DyB₂C₂ as a function of incident x-ray energy, temperature and azimuthal angle. The results show that the transition at T_Q is caused by the ordering of the quadrupolar moments. In addition, we have found that the structural phase transition occurs at T_Q concomitantly. A structural model for the AFQ ordering, for which the propagation vectors are (0, 0, 1/2) and (0, 1, 1/2), is also presented.

The authors wish to thank Professor H Shiba for valuable discussions.

Note added in proof. Quite recently, we realized that Hirota *et al* [11] had carried out similar experiments on DyB₂C₂; however, they don't determine the AFQ ordering pattern.

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