

Ordered Charge Asphericity around Dysprosium and Structural Deformation in DyB₂C₂

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The orbitally ordered phase of DyB₂C₂ has been studied by nonresonant x-ray diffraction with high-brilliance synchrotron radiation. From the condition of diffraction, the symmetry property of the charge distribution around dysprosium has been concluded at the quadrupolar level. The quantitative inspection, furthermore, indicates that the observed signals cannot be interpreted as arising only from the 4*f* electrons of dysprosium responsible for the ordering; instead, the experiment can be described rather well by considering a distortion of the metalloid network concomitant with the ordering.

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Recently, the observation of the so-called antiferroquadrupolar (AFQ) ordering of DyB₂C₂ has been reported by two different groups [1,2]. Though so far the existence of the AFQ ordering of the atomic 4*f* electrons, where the aspherical charge densities are in spatial order so as to form the superlattice, has been supported by many experiments on some rare-earth compounds, the x-ray diffraction from this charge modulation had not been measured. This is possibly because the available sample with a relatively high ordering temperature had not been found and also it has been believed that the superlattice signals might be too weak to be captured by the ordinary x-ray diffraction techniques. The above two groups, making use of the enhancement of the anisotropy in the x-ray susceptibility near the absorption edges [3–5], successfully measured the superlattice reflections from DyB₂C₂, having a highest ordering temperature T_Q hitherto known of about 25 K [6], and then argued the model structure of the AFQ ordering, the thermal variation of the order parameter, and so on.

In spite of such an apparent success, the observed phenomena seem difficult to be fully understood from the microscopic point of view, because the resonance method they adopted involves the excited states of the electron system during the scattering process and the tensorial property of the x-ray susceptibility in the vicinity of the absorption edges, essential to their experiments,

is just treated qualitatively. Thus, though the existence of the AFQ ordering has been certainly proved, the magnitude and the orientation of the charge asphericity is still an open question. On the other hand, at least in theory, the superlattice and forbidden reflections, which do not appear as long as the scattering factors are identical for the same elements in the crystal and independent of the sites, should occur for the AFQ-ordered state even on the nonresonant condition too, and, if detectable, give us the detailed information about the ordered charge distribution. In the following, at first, considering the lowest order (quadrupolar) charge asphericity, let us have a look at the relation between the symmetry and the expected extinction rules in the conventional nonresonant x-ray diffraction, and illustrate at which reflection indices should be aimed with this approach. Though neglected here for simplicity and brevity of space, the terms arising from higher-order charge asphericity beyond the quadrupolar one might also be important in some realistic cases. We shall return to this point in the latter part of the paper.

The operator for the x-ray atomic scattering factor is described by $\sum_{\nu} \exp(i\mathbf{k} \cdot \mathbf{r}_{\nu})$, where \mathbf{k} is the x-ray scattering vector and \mathbf{r}_{ν} is the position of the ν th electron. For the rare-earth ions, taking the summation with respect to the 4*f* electrons, which seem substantial to the anisotropy, the following expression is obtained for a manifold of states with the quantum number of the total angular momentum J being constant [7]:

$$\sum_{\nu=4f} \exp(i\mathbf{k} \cdot \mathbf{r}_{\nu}) = n_{4f} \langle j_0 \rangle - 5\alpha_J \langle j_2 \rangle \left\{ \frac{1}{4} (3 \cos^2 \beta - 1) O_2^0 + 3 \sin \beta \cos \beta \cos \gamma O_{2x} + 3 \sin \beta \cos \beta \sin \gamma O_{2y} + \frac{3}{4} \sin^2 \beta \cos 2\gamma O_2^2 + \frac{3}{2} \sin^2 \beta \sin 2\gamma O_{2xy} \right\}, \quad (1)$$

where n_{4f} is the number of the 4*f* electron, $\langle j_n \rangle$ is the 4*f* radial integral of the n th order spherical Bessel function $j_n(kr)$, and β , γ describe the polar coordinates of the direction of the x-ray scattering vector in the x , y , z

frame. O_2^0 , O_2^2 , and O_{ij} ($i, j = x, y, z$) denote the operators written by the total angular momentum operator \mathbf{J} , defined as

$$O_2^0 = 3J_z^2 - J(J+1), \quad O_2^x = J_x^2 - J_y^2, \quad (2)$$

$$O_{ij} = \frac{1}{2}(J_i J_j + J_j J_i),$$

and α_J in Eq. (1) is the so-called Stevens parameter of the second order, which is a constant depending on the rare earths. The diffraction intensity expected for the superlattice or forbidden reflection ascribed to the AFQ ordering is proportional to the square of the thermal average of the anisotropic part of the scattering factor, and hence directly related to the aspherical distortion of the $4f$ charge cloud. Note that the thermal average of O_2^z and O_{xy} , for example, correspond to the quadrupolar distortion of the type of $\sum_\nu (x_\nu^2 - y_\nu^2)$ and $\sum_\nu x_\nu y_\nu$, respectively. From Eq. (1), this AFQ signal is estimated to be very weak but adequately within reach

of the existing synchrotron-radiation sources in favorable cases.

DyB₂C₂ has the tetragonal structure with the alternate stacking of the dysprosium layer and the boron-carbon network one along the c axis. The AFQ-structure pattern in this material has been proposed by Tanaka *et al.* [1], where the local $+x$ directions for the dysprosium atoms at the (000), $(\frac{1}{2}\frac{1}{2}0)$, (001), and $(\frac{1}{2}\frac{1}{2}1)$ sites of the tetragonal unit cell, hereafter denoted by the subscripts 1 ~ 4, are at angles of ϕ , $\frac{\pi}{2} - \phi$, $\frac{\pi}{2} + \phi$, and $\pi - \phi$, respectively, from the crystallographic a axis, and the $+z$ directions are parallel to the c axis at all sites (Fig. 1). Assuming that the dysprosium atom on each site has the same charge asphericity except for the orientation and applying Eq. (1) to this model structure, the scattering amplitudes of the superlattice reflections with half-odd integer l are calculated to be

$$F_{h+k=\text{odd}} \propto f_1 - f_2 - f_3 + f_4 = -5\alpha_J \langle j_2 \rangle \frac{1}{K^2} \left\{ -6kl \frac{a}{c} (\cos\phi - \sin\phi) \langle O_{zx} \rangle_T + 6hl \frac{a}{c} (\cos\phi - \sin\phi) \langle O_{yz} \rangle_T \right. \\ \left. + 3(h^2 - k^2) \cos 2\phi \langle O_2^z \rangle_T + 12hk \cos 2\phi \langle O_{xy} \rangle_T \right\}, \quad (3)$$

$$F_{h+k=\text{even}} \propto f_1 + f_2 - f_3 - f_4 = -5\alpha_J \langle j_2 \rangle \frac{1}{K^2} \left\{ 6hl \frac{a}{c} (\cos\phi + \sin\phi) \langle O_{zx} \rangle_T + 6kl \frac{a}{c} (\cos\phi + \sin\phi) \langle O_{yz} \rangle_T \right. \\ \left. + 6hk \sin 2\phi \langle O_2^z \rangle_T - 6(h^2 - k^2) \sin 2\phi \langle O_{xy} \rangle_T \right\}, \quad (4)$$

where f_i is the atomic scattering factor of dysprosium on site i , $K^2 = h^2 + k^2 + (\frac{a}{c}l)^2$, and $\langle \cdots \rangle_T$ denotes the thermal average. Similarly, the scattering amplitudes of the forbidden reflections with $h+k = \text{odd}$ and $l = \text{integer}$ are expressed as

$$F \propto f_1 - f_2 + f_3 - f_4 = -5\alpha_J \langle j_2 \rangle \frac{1}{K^2} \left\{ 6hl \frac{a}{c} (\cos\phi - \sin\phi) \langle O_{zx} \rangle_T + 6kl \frac{a}{c} (\cos\phi - \sin\phi) \langle O_{yz} \rangle_T \right\}. \quad (5)$$

Considering the symmetry of the crystal, furthermore, it is predicted that $\langle O_{zx} \rangle_T = \langle O_{yz} \rangle_T = 0$ and also that either $\langle O_{xy} \rangle_T$ or $\langle O_2^z \rangle_T$ should be zero; thereby Eqs. (3)–(5) become very simple.

Now, our tentative experimental plan can be summed up as follows. (i) It should be confirmed that the (00 l) superlattice reflection does not occur, for $f_{1\sim 4}$ are equivalent to each other for this type of reflection with $\beta_{1\sim 4} = 0$, as long as the dysprosium atom on each site has the same charge asphericity. (ii) It should be also confirmed that the forbidden reflection does not arise, i.e., $\langle O_{zx} \rangle_T = \langle O_{yz} \rangle_T = 0$. Since, on the forbidden condition of $h+k = \text{odd}$ and $l = \text{integer}$, the multiple scattering may cause a diffraction, this effect has to be carefully avoided by the sample rotation about the scattering vector, or the origin of the observed signal, if any, has to be specified with some additional measurements. (iii) If the results of the above measurements are favorable, we can know whether $\langle O_{xy} \rangle_T = 0$ or not by examining the superlattice reflection for $h = 0$ and $k = \text{even}$. Also, we can check whether $\langle O_2^z \rangle_T = 0$ or not by the measurement of the (hhl) superlattice reflection, where $h \neq 0$. (iv) Combining the scattering amplitudes obtained for

the superlattice reflections with $h+k = \text{odd}$ and even, we can finally get information about the magnitude and the orientation of the charge asphericity in question.

Experiments were done at the undulator beam line 46XU of SPring-8, where one of the most intense synchrotron radiations at present is available. The energy of the incident beam was tuned to be 20 keV by the double-crystal monochromator with Si(111) and the higher-order component especially of 40 keV was reduced as much as possible by the platinum-coated mirror. Figure 2 shows the l -scan results measured at 18 K, well below the AFQ-ordering temperature T_Q of 25 K and above the magnetic transition point T_N of 16 K [6]. Here, the (014) forbidden reflection shown in Fig. 2(b) does not seem to be of the AFQ origin but of the multiple-scattering one, because the peak does not vanish even at 30 K and the intensity is disorderly dependent on the azimuthal rotation of the sample. It can be thus concluded from these results with the aforementioned theoretical consideration that the charge density around the dysprosium nucleus is distorted within the c plane in the O_2^z type, that is, the thermal average of $\sum_\nu (x_\nu^2 - y_\nu^2)$ is finite.

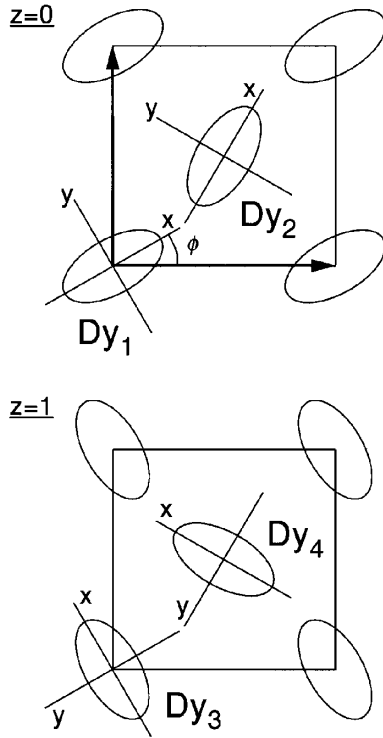


FIG. 1. Schematic diagrams of the $z = 0$ and $z = 1$ sections of the AFQ-ordered DyB_2C_2 crystal. The present experiments have indicated that the charge around dysprosium is distorted such that the thermal average of $\sum_{\nu}(x_{\nu}^2 - y_{\nu}^2)$ is finite. Bold arrows show crystallographic axes.

From the quantitative point of view, however, the observed phenomena require more careful examination. Figure 3(a) shows the temperature dependences of the scattering amplitudes for the $(01\frac{1}{2})$, $(11\frac{1}{2})$, and $(12\frac{1}{2})$ reflections, which are 1 or 2 orders of magnitude larger than the values expected from Eqs. (3) and (4). Figure 3(b) displays the scattering amplitudes for the $(01\frac{n}{2})$, $(11\frac{n}{2})$, and $(12\frac{n}{2})$ ($n = 7, 9, 11, 13$) reflections at 18 K as a function of $q = \frac{k}{2a}$. This q dependence too, which little reduces as q increases, is not consistent with the behavior of the diffraction from quadrupolar charge distortion. According to Eqs. (3) and (4), the scattering amplitudes of these reflections are to be proportional to $\sin 2\phi \langle O_2^2 \rangle_T$ or $\cos 2\phi \langle O_2^2 \rangle_T$, and, if so, the value and the thermal variation of ϕ and $\langle O_2^2 \rangle_T$ could be determined from the results. But, the above findings indicate that the problem is not so simple. What is the source of this discrepancy?

In the first place, as is mentioned before, we should note here that, despite the prevalent word of *quadrupolar* ordering, higher-order charge asphericity having the same symmetry can also exist [9], which may contribute to the superlattice signals as much as the quadrupolar distortion especially for high- q reflections. But, even taking into account these contributions, the scattering amplitude estimated is still too small to meet the quantitative success.

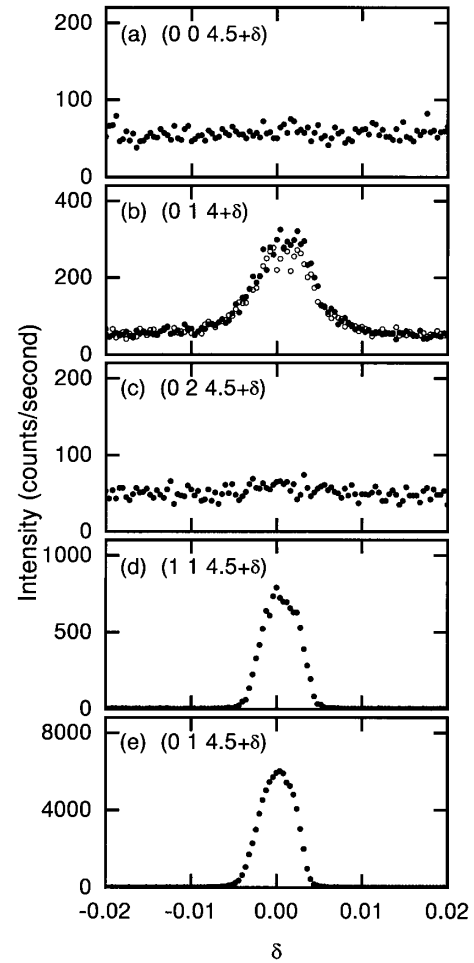


FIG. 2. The raw data of the l -scan measurements for various types of reflections. Data were taken at 18 K except the ones denoted by open circles in (b), which were taken at 30 K.

In the second place, it should be also noted that the atomic displacement might take place concomitantly with the AFQ ordering. Assuming the displacement of the surrounding boron and carbon atoms as proposed by Tanaka *et al.* [1], the scattering amplitude from the boron (carbon) part are calculated to be

$$F_{B(C)} \propto 8f_{B(C)} \sin \pi l \sin 2\pi l \delta_{B(C)} \times \sin \pi \left[\frac{h}{2} + k \left(\frac{1}{2} - 2x_{B(C)} \right) \right] \times \sin \pi \left[-h \left(\frac{1}{2} - 2x_{B(C)} \right) + \frac{k}{2} \right] \quad (6)$$

for half-odd integer l , where δ is the displacement along the c axis, x is the positional parameter ($x_B = 0.363$ and $x_C = 0.161$) [6], and f is the atomic scattering factor (neglecting the site dependence for the present). According to this idea, as shown in Fig. 3(b), the experimental results can be described rather well by a deformation of the metalloid network as in the inset. Such a

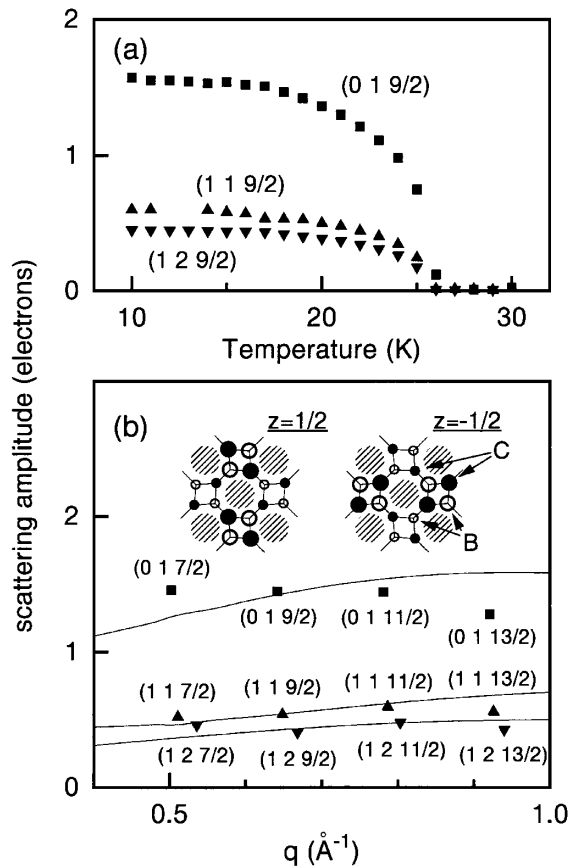


FIG. 3. Scattering amplitudes of some superlattice reflections per AFQ-ordered unit cell of DyB_2C_2 containing 4 formula units. (a) shows the temperature dependences for the $(01\frac{9}{2})$, $(11\frac{9}{2})$, and $(12\frac{9}{2})$ reflections, from which we can see that these reflections properly accompany the AFQ transition. (b) shows the $q = \frac{k}{2a}$ dependences for the $(01\frac{n}{2})$, $(11\frac{n}{2})$, and $(12\frac{n}{2})$ ($n = 7, 9, 11, 13$) reflections at 18 K. The intensity of each reflection is scaled with fitting the scattering amplitudes for the $(11n)$ ($n = 4, 5, 6, 7$) fundamental reflections by the theoretical q dependence [8], the measurement of which doubles as a check on the extinction effect. Solid curves in (b) indicate the scattering amplitudes due to the modulated boron-carbon layers as shown in the inset, where empty circles and solid circles represent the boron and carbon atoms, and large (small) ones mean that the atoms move upward (downward) along the c axis. Here, the isotropic (spherically averaged) values are used for the atomic scattering factors and the magnitudes of the displacements are set to be 0.011 \AA and 0.016 \AA for boron and carbon, respectively; accordingly note that these estimates for the displacements may be somewhat changed by considering directional bonding nature and vibration characteristics of the atoms forming the two dimensional network. Hatched areas denote the positions of the dysprosium atoms projected onto the $z = \pm \frac{1}{2}$ planes.

modification of the atomic configuration might mediate the coupling between the aspherical charge densities of the neighboring dysprosium atoms, though no appreciable anomaly in lattice constant seems to macroscopically follow upon the ordering [2,6].

Resultingly, the present series of measurements appeared to probe the signals where the contribution of the charge asphericity in dysprosium is quite small compared to the other contribution. Nevertheless, in the light of the compatibility between the electron orbitals and the surrounding lattice distortion, for example, it seems safe to say that the charge distribution around dysprosium is of the $O_2^2(x^2 - y^2)$ type and is arranged in the crystal as schematically shown in Fig. 1 in the AFQ-ordered state. More decisive knowledge about the aspherical charge of dysprosium may be brought by the measurements of the planes close to the $\langle 001 \rangle$ zone, such as $(06\frac{1}{2})$, $(07\frac{1}{2})$, and $(55\frac{1}{2})$, where the scattering amplitude due to the asphericity should be much larger owing to the geometrical factor and, on the other hand, the amplitude of Eq. (6) is reduced by the factor of $\sin 2\pi l\delta$. Another important implication of this study is the structural deformation associated with the AFQ transition, a good understanding of which would be the key to the interaction mechanism and high T_Q of this compound. The effect of the structural change might also have to be properly assessed to extract information about the orbital ordering from the resonant-scattering data [10]. Further investigation with full structure analysis will be an interesting subject in the future.

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