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Effect of Crystalline Electric Field on Magnetic Anisotropy of Nd_2BaNiO_5

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We have investigated magnetic anisotropy energy of the antiferromagnetic Nd_2BaNiO_5(T_N =48K) caused by the crystalline electric field. For Ni^{2+} ion, by calculating the crystalline electric field at Ni ion site the energy level splitting of the orbital state of Ni^{2+} ion (^3F) has been obtained. We have derived the Pryce's spin Hamiltonian and evaluated the single-ion-type anisotropy constants. The result shows that the easy direction of the spin moment of Ni^{2+} ion is parallel to the *a*-axis. For Nd^{3+} ion the crystalline electric field at Nd ion site has been calculated. By the use of operator equivalents method, we have obtained the effective Hamiltonian for the total angular momentum J of Nd^{3+} ion ($^4I_{9/2}$). The result indicates that the easy direction of Nd's magnetic moment ($= -g_J J \mu_B$) is parallel to the *c*-axis. These calculated results are discussed in connection with observations.

1 Introduction

Nd_2BaNiO_5 is an antiferromagnet below T_N=48K [1]. The crystal structure of this compound (see Fig.1) is similar to that of Y_2BaNiO_5 which is well known as one-dimensional Haldane system. In Y_2BaNiO_5 the non-magnetic Y^{3+} ion is intervened between one-dimensional NiO_6 chains. By replacing Y^{3+} in Y_2BaNiO_5 by the magnetic Nd^{3+}, a magnetic coupling is caused between the NiO_6 chains and then three-dimensional magnetic ordering occurs in Nd_2BaNiO_5. For a single crystal of Nd_2BaNiO_5 the antiferromagnetic ordering was observed by the neutron diffraction measurement, and the direction of magnetic moment was found to be along the *c*-axis for Nd^{3+} and tilted from the *c*-axis to the *a*-axis by the angle of about 35° for Ni [2]. Okubo *et al.* measured the magnetization process under the external field applied along the *c*-axis and found two kinds of the metamagnetic transition. They reported that the easy direction of the total magnetic moment of Nd_2BaNiO_5 is parallel to the *c*-axis [3].

In this paper we investigate the single-ion-type magnetic anisotropy of Ni^{2+} and Nd^{3+} ions of Nd_2BaNiO_5 caused by the crystalline electric field. The case of Ni^{2+} ion and that of Nd^{3+} ion are studied in 2 and 3, respectively.

2 The case of Ni^{2+} ion.

The Crystalline electric field for one 3d electron of Ni^{2+} ion, arising from the 1st, 2nd, $\cdots$ neighboring ions, can be expressed as

$$V(r,\theta,\phi) = \sum_{m=0,\pm 2} A_{2m} r^2 Y_{2m}(\theta,\phi) + \sum_{m=0,\pm 2,\pm 4} A_{4m} r^4 Y_{4m}(\theta,\phi), \qquad (2.1)$$

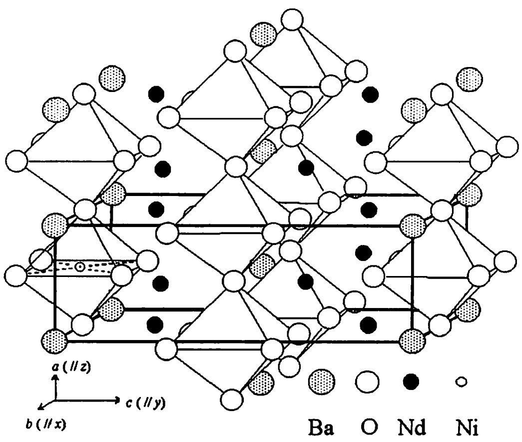

Figure 1: Crystal structure of Nd_2BaNiO_5.

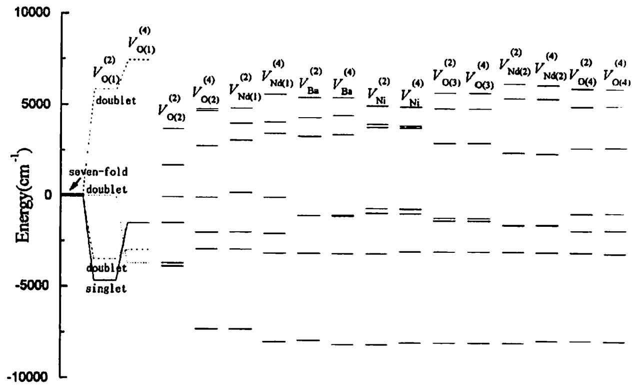

Figure 2: Orbital level splitting of Ni^{2+}.

where the polar coordinate (r, θ, φ) with the polar axis (z) parallel to the a-axis is used and the azimuthal angle is measured from the b-axis (x). A_{20} etc. are obtained as

$$
\begin{aligned}
A_{20} &= \sqrt{\frac{16\pi}{5}}\left(\frac{-2e}{R_1^3}\right) - \sqrt{\frac{16\pi}{5}}\sum_{j=2,8}\left(\frac{-2e}{R_j^3}\right) + \sqrt{\frac{16\pi}{5}}\left(\frac{3e}{R_3^3}\right)\left(2\cos^2\Theta_3 - \sin^2\Theta_3\right) \\
&+ \sqrt{\frac{16\pi}{5}}\left(\frac{2e}{R_4^3}\right)\left(2\cos^2\Theta_4 - \sin^2\Theta_4\right) + \sqrt{\frac{16\pi}{5}}\left(\frac{2e}{R_5^3}\right) \\
&+ \sqrt{\frac{64\pi}{5}}\left(\frac{-2e}{R_6^3}\right)\left(2\cos^2\Theta_6 - \sin^2\Theta_6\right) - \sqrt{\frac{16\pi}{5}}\left(\frac{3e}{R_7^3}\right) \\
A_{22} &= \sqrt{\frac{24\pi}{5}}\sum_{j=2,8}\left(\frac{-2e}{R_j^3}\right)\cos 2\Phi_j - \sqrt{\frac{24\pi}{5}}\left(\frac{3e}{R_3^3}\right)\sin^2\Theta_3 + \sqrt{\frac{24\pi}{5}}\left(\frac{2e}{R_4^3}\right)\sin^2\Theta_4 \\
&+ \frac{4\sqrt{6\pi}}{\sqrt{5}}\left(\frac{-2e}{R_6^3}\right)\sin^2\Theta_6\cos 2\Phi_6 + \sqrt{\frac{24\pi}{5}}\left(\frac{3e}{R_7^3}\right)\cos 2\Phi_7 \\
A_{2-2} &= A_{22}
\end{aligned}
$$

$$
\begin{aligned}
A_{40} &= \frac{4\sqrt{\pi}}{3}\left(\frac{-2e}{R_1^5}\right) + \sqrt{\pi}\sum_{j=2,8}\left(\frac{-2e}{R_j^5}\right) + \frac{\sqrt{\pi}}{3}\left(\frac{3e}{R_3^5}\right)\left(35\cos^4\Theta_3 - 30\cos^2\Theta_3 + 3\right) \\
&+ \frac{\sqrt{\pi}}{3}\left(\frac{2e}{R_4^5}\right)\left(35\cos^4\Theta_4 - 30\cos^2\Theta_4 + 3\right) + \frac{4\sqrt{\pi}}{3}\left(\frac{2e}{R_5^5}\right) \\
&+ \frac{2\sqrt{\pi}}{3}\left(\frac{-2e}{R_6^5}\right)\left(35\cos^4\Theta_6 - 30\cos^2\Theta_6 + 3\right) + \sqrt{\pi}\left(\frac{3e}{R_7^5}\right) \\
A_{42} &= -\sqrt{\frac{10\pi}{9}}\sum_{j=2,8}\left(\frac{-2e}{R_j^5}\right)\cos 2\Phi_j - \sqrt{\frac{10\pi}{9}}\left(\frac{3e}{R_3^5}\right)\left\{\sin^2\Theta_3\left(7\cos^2\Theta_3 - 1\right)\right\} \\
&+ \sqrt{\frac{10\pi}{9}}\left(\frac{2e}{R_4^5}\right)\left\{\sin^2\Theta_4\left(7\cos^2\Theta_4 - 1\right)\right\} + \frac{4\sqrt{5\pi}}{3\sqrt{2}}\left(\frac{-2e}{R_6^5}\right)\sin^2\Theta_6\left(7\cos^2\Theta_6 - 1\right)\cos 2\Phi_6 \\
&- \sqrt{\frac{10\pi}{9}}\left(\frac{3e}{R_7^5}\right)\cos 2\Phi_7 \\
A_{4-2} &= A_{42}
\end{aligned}
$$

$$
\begin{aligned}
A_{44} &= \frac{\sqrt{35\pi}}{3\sqrt{2}} \sum_{j=2,8} \left(\frac{-2e}{R_j^5}\right) \cos 4\Phi_j + \frac{\sqrt{35\pi}}{3\sqrt{2}} \left(\frac{3e}{R_3^5}\right) \sin^4 \Theta_3 + \frac{\sqrt{35\pi}}{3\sqrt{2}} \left(\frac{2e}{R_4^5}\right) \sin^4 \Theta_4 \\
&+ \frac{\sqrt{70\pi}}{3} \left(\frac{-2e}{R_6^5}\right) \sin^4 \Theta_6 \cos 4\Phi_6 + \frac{\sqrt{35\pi}}{3\sqrt{2}} \left(\frac{3e}{R_7^5}\right) \cos 4\Phi_7 \\
A_{4-4} &= A_{44},
\end{aligned}
\tag{2.2}
$$

where (R_i, Θ_i, Φ_i) denotes the i-th neighbor's ion coordinate and i=1,2 for Oxygen, i=3 for Nd, i=4 for Ba, i=5 for Ni, i=6 for O, i=7 for Nd, i=8 for O are used.

The free Ni^{2+} ion has eight 3d electrons. In this case Ni^{2+} ion can be treated as the ion having two d electrons with positive charge. The lowest multiplet of Ni^{2+} ion is ^3F which has seven-fold orbital degeneracy and orbital functions are expressed as $\Psi_{3\pm3}$, $\Psi_{3\pm2}$, $\Psi_{3\pm1}$, Ψ_{30}, where the first and second suffixes of Ψ denote the orbital quantum number and the orbital magnetic quantum number. In order to obtain the orbital level splitting in the crystal we have calculated the matrix elements of $e\sum_{i=1,2} V(r_i, \theta_i, \varphi_i)(e > 0)$ with respect to the seven orbital functions. The orbital level splitting and the wave function of each level calculated by taking account of the crystalline electric field arising from the 1st nearest neighbor to the 8th neighbor ions, successively, are shown in Fig.2. Here we used $< r^2 >$=2.21a.u. and $< r^4 >$=7.85a.u.. These values are calculated by using Slater's semiempirical function for the 3d radial function of Ni^{2+}. The ground state is given by $0.7065(\Psi_{32}+\Psi_{3-2})$-$0.0409\Psi_{30}$, where the wave function $(\Psi_{32} + \Psi_{3-2})$ is extended toward the nearest neighboring four oxygen ions in the bc-plane. The energy separation between the ground state and the 1st excited states is roughly 5000cm^{-1}. On the basis of the obtained orbital level splitting, we have derived the spin Hamiltonian [4] in the following form :

$$
H_S = DS_z^2 + E(S_x^2 - S_y^2), \tag{2.3}
$$

where

$$
D = -\lambda^2 \left\{ \Lambda_z - \frac{1}{2}(\Lambda_x + \Lambda_y) \right\} \tag{2.4}
$$

$$
E = -\frac{\lambda^2}{2}(\Lambda_x - \Lambda_y) \tag{2.5}
$$

with

$$
\Lambda_{\mu\nu} = \sum_{e\neq g} \frac{< g|L_\mu|e >< e|L_\nu|g >}{E_e - E_g}. \tag{2.6}
$$

λ is the spin-orbit coupling coefficient, and E_g and E_e are energy values of the ground and excited states, respectively. L_z, L_x and L_y have matrix elements between the ground state and the 1st, 3rd and 5th, 2nd and 5th excited states, respectively. D and E are evaluated as

$$
\begin{aligned}
D &= -0.00025\lambda^2 \mathrm{cm}^{-1} = -28.06\mathrm{cm}^{-1} \\
E &= 0.00011\lambda^2 \mathrm{cm}^{-1} = 12.34\mathrm{cm}^{-1}.
\end{aligned}
$$

Here $\lambda = -335\mathrm{cm}^{-1}$ for the free Ni^{2+} ion is used. The negative sign of D means that the easy direction of spin of Ni^{2+} is parallel to the z-axis (// a-axis). This result is consistent with the case of Y_2BaNiO_5 [5] which has a similar crystal structure and almost the same lattice constants to those of Nd_2BaNiO_5. In Nd_2BaNiO_5, however, the neutron diffraction measurement reported that the magnetic moment of Ni is tilted from the a-axis toward the c-axis by the angle ~55° [2]. To determine the easy direction of Ni moment a coupling between Ni and Nd moments is important.

3 The case of Nd^{3+} ion

The crystalline electric field acting on one electron at Nd^{3+} ion site, which arises from the neighboring oxygen, Ba, Nd and Ni ions, is given by

$$\begin{aligned} V(r,\theta,\phi) &= \sum_{m=\pm1} B_{1m} r Y_{1m}(\theta,\phi) + \sum_{m=0,\pm2} B_{2m} r^2 Y_{2m}(\theta,\phi) \\ &+ \sum_{m=\pm1,\pm3} B_{3m} r^3 Y_{3m}(\theta,\phi) + \sum_{m=0,\pm2,\pm4} B_{4m} r^4 Y_{4m}(\theta,\phi) \\ &+ \sum_{m=\pm1,\pm3,\pm5} B_{5m} r^5 Y_{5m}(\theta,\phi) + \sum_{m=0,\pm2,\pm4,\pm6} B_{6m} r^6 Y_{6m}(\theta,\phi), \end{aligned} \tag{3.1}$$

where the polar coordinate with the polar axis (z) parallel to the a-axis is used and B_{20} etc. are obtained as follows:

$$\begin{aligned} B_{11} &= \sqrt{\frac{8\pi}{3}}i\left(\frac{-2e}{R_1^2}\right)\sin\Phi_1 - \frac{1}{2}\sqrt{\frac{8\pi}{3}}i\left(\frac{-2e}{R_2^2}\right) + 2\sqrt{\frac{8\pi}{3}}i\left(\frac{-2e}{R_3^2}\right)\sin\Theta_3\sin\Phi_3 - \frac{2\sqrt{8\pi}}{3}i\left(\frac{2e}{R_4^2}\right)\sin\Theta_4 \\ &+ 2\sqrt{\frac{8\pi}{3}}i\left(\frac{3e}{R_5^2}\right)\sin\Theta_5\sin\Phi_5 + \sqrt{\frac{8\pi}{3}}i\left(\frac{2e}{R_6^2}\right)\sin\Phi_6 + \cdots \end{aligned}$$

$$B_{1-1} = B_{11}$$

$$\begin{aligned} B_{20} &= -\sqrt{\frac{4\pi}{5}}\left(\frac{-2e}{R_1^3}\right) - \sqrt{\frac{\pi}{5}}\left(\frac{-2e}{R_2^3}\right) + \sqrt{\frac{16\pi}{5}}\left(\frac{-2e}{R_3^3}\right)(2\cos^2\Theta_3 - \sin^2\Theta_3) \\ &+ \sqrt{\frac{4\pi}{5}}\left(\frac{2e}{R_4^3}\right)(2\cos^2\Theta_4 - \sin^2\Theta_4) + \sqrt{\frac{16\pi}{5}}\left(\frac{3e}{R_5^3}\right)(2\cos^2\Theta_5 - \sin^2\Theta_5) \\ &- \sqrt{\frac{4\pi}{5}}\left(\frac{2e}{R_6^3}\right) + \sqrt{\frac{16\pi}{5}}\left(\frac{3e}{R_7^3}\right) + \cdots \end{aligned}$$

$$\begin{aligned} B_{22} &= \sqrt{\frac{6\pi}{5}}\left(\frac{-2e}{R_1^3}\right)\cos 2\Phi_1 - \sqrt{\frac{3\pi}{10}}\left(\frac{-2e}{R_2^3}\right) + \sqrt{\frac{24\pi}{5}}\left(\frac{-2e}{R_3^3}\right)\sin^2\Theta_3\cos 2\Phi_3 \\ &- \sqrt{\frac{6\pi}{5}}\left(\frac{2e}{R_4^3}\right)\sin^2\Theta_4 + \sqrt{\frac{24\pi}{5}}\left(\frac{3e}{R_5^3}\right)\sin^2\Theta_5\cos 2\Phi_5 + \sqrt{\frac{6\pi}{5}}\left(\frac{2e}{R_6^3}\right)\cos 2\Phi_6 - \cdots \end{aligned}$$

$$B_{2-2} = B_{22}$$

$$\begin{aligned} B_{31} &= -\sqrt{\frac{3\pi}{7}}i\left(\frac{-2e}{R_1^4}\right)\sin\Phi_1 + \frac{\sqrt{21\pi}}{14}i\left(\frac{-2e}{R_2^4}\right) + \frac{2\sqrt{21\pi}}{7}i\left(\frac{-2e}{R_3^4}\right)\sin\Theta_3\left(5\cos^2\Theta_3 - 1\right)\sin\Phi_3 \\ &- \frac{\sqrt{21\pi}}{7}i\left(\frac{2e}{R_4^4}\right)\sin\Theta_4\left(5\cos^2\Theta_4 - 1\right) + \frac{2\sqrt{21\pi}}{7}i\left(\frac{3e}{R_5^4}\right)\sin\Theta_5\left(5\cos^2\Theta_5 - 1\right)\sin\Phi_5 \\ &- \sqrt{\frac{3\pi}{7}}i\left(\frac{2e}{R_6^4}\right)\sin\Phi_6 + \cdots \end{aligned}$$

$$B_{3-1} = B_{31}$$

$$\begin{aligned} B_{33} &= \sqrt{\frac{5\pi}{7}}i\left(\frac{-2e}{R_1^4}\right)\sin 3\Phi_1 + \frac{\sqrt{35\pi}}{14}i\left(\frac{-2e}{R_2^4}\right) + \frac{2\sqrt{35\pi}}{7}i\left(\frac{-2e}{R_3^4}\right)\sin^3\Theta_3\sin 3\Phi_3 \\ &+ \frac{\sqrt{35\pi}}{7}i\left(\frac{2e}{R_4^4}\right)\sin^3\Theta_4 + \frac{2\sqrt{35\pi}}{7}i\left(\frac{3e}{R_5^4}\right)\sin^3\Theta_5\sin 3\Phi_5 + \sqrt{\frac{5\pi}{7}}i\left(\frac{2e}{R_6^4}\right)\sin 3\Phi_6 - \cdots \end{aligned}$$

$$B_{3-3} = B_{33}$$

$$
\begin{aligned}
B_{40} = & \frac{\sqrt{\pi}}{2}\left(\frac{-2e}{R_1^5}\right) + \frac{\sqrt{\pi}}{4}\left(\frac{-2e}{R_2^5}\right) + \frac{\sqrt{\pi}}{3}\left(\frac{-2e}{R_3^5}\right)\left(35\cos^4\Theta_3 - 30\cos^2\Theta_3 + 3\right) \\
& + \frac{\sqrt{\pi}}{6}\left(\frac{2e}{R_4^5}\right)\left(35\cos^4\Theta_4 - 30\cos^2\Theta_4 + 3\right) + \frac{\sqrt{\pi}}{3}\left(\frac{3e}{R_5^5}\right)\left(35\cos^4\Theta_5 - 30\cos^2\Theta_5 + 3\right) \\
& + \frac{\sqrt{\pi}}{2}\left(\frac{2e}{R_6^5}\right) + \frac{4\sqrt{\pi}}{3}\left(\frac{3e}{R_7^5}\right) + \cdots \\
B_{42} = & -\frac{\sqrt{10\pi}}{6}\left(\frac{-2e}{R_1^5}\right)\cos 2\Phi_1 + \frac{\sqrt{10\pi}}{12}\left(\frac{-2e}{R_2^5}\right) + \sqrt{\frac{10\pi}{9}}\left(\frac{-2e}{R_3^5}\right)\sin^2\Theta_3\left(7\cos^2\Theta_3 - 1\right)\cos 2\Phi_3 \\
& - \frac{\sqrt{10\pi}}{6}\left(\frac{2e}{R_4^5}\right)\sin^2\Theta_4\left(7\cos^2\Theta_4 - 1\right) + \sqrt{\frac{10\pi}{9}}\left(\frac{3e}{R_5^5}\right)\sin^2\Theta_5\left(7\cos^2\Theta_5 - 1\right)\cos 2\Phi_5 \\
& - \frac{\sqrt{10\pi}}{6}\left(\frac{2e}{R_6^5}\right)\cos 2\Phi_6 - \cdots \\
B_{4-2} = & B_{42} \\
B_{44} = & \frac{\sqrt{70\pi}}{12}\left(\frac{-2e}{R_1^5}\right)\cos 4\Phi_1 + \frac{\sqrt{70\pi}}{24}\left(\frac{-2e}{R_2^5}\right) + \frac{\sqrt{70\pi}}{6}\left(\frac{-2e}{R_3^5}\right)\sin^4\Theta_3\cos 4\Phi_3 \\
& + \frac{\sqrt{70\pi}}{12}\left(\frac{2e}{R_4^5}\right)\sin^4\Theta_4 + \frac{\sqrt{70\pi}}{6}\left(\frac{3e}{R_5^5}\right)\sin^4\Theta_5\cos 4\Phi_5 + \frac{\sqrt{70\pi}}{12}\left(\frac{2e}{R_6^5}\right)\cos 4\Phi_6 + \cdots \\
B_{4-4} = & B_{44}
\end{aligned}
$$

$$
\begin{aligned}
B_{51} = & \frac{1}{4}\sqrt{\frac{30\pi}{11}}i\left(\frac{-2e}{R_1^6}\right)\sin\Phi_1 - \frac{1}{8}\sqrt{\frac{30\pi}{11}}i\left(\frac{-2e}{R_2^6}\right) \\
& + \sqrt{\frac{5\pi}{66}}i\left(\frac{-2e}{R_3^6}\right)\sin\Theta_3\left(63\cos^4\Theta_3 - 42\cos^2\Theta_3 + 3\right)\sin\Phi_3 \\
& - \frac{1}{2}\sqrt{\frac{5\pi}{66}}i\left(\frac{2e}{R_4^6}\right)\sin\Theta_4\left(63\cos^4\Theta_4 - 42\cos^2\Theta_4 + 3\right) \\
& + \sqrt{\frac{5\pi}{66}}i\left(\frac{3e}{R_5^6}\right)\sin\Theta_5\left(63\cos^4\Theta_5 - 42\cos^2\Theta_5 + 3\right)\sin\Phi_5 \\
& + \frac{1}{4}\sqrt{\frac{30\pi}{11}}i\left(\frac{2e}{R_6^6}\right)\sin\Phi_6 + \cdots \\
B_{5-1} = & B_{51} \\
B_{53} = & -\frac{1}{4}\sqrt{\frac{35\pi}{11}}i\left(\frac{-2e}{R_1^6}\right)\sin 3\Phi_1 - \frac{1}{8}\sqrt{\frac{35\pi}{11}}i\left(\frac{-2e}{R_2^6}\right) + \sqrt{\frac{35\pi}{44}}i\left(\frac{-2e}{R_3^6}\right)\sin^3\Theta_3\left(9\cos^2\Theta_3 - 1\right)\sin 3\Phi_3 \\
& + \frac{1}{4}\sqrt{\frac{35\pi}{11}}i\left(\frac{2e}{R_4^6}\right)\sin^3\Theta_4\left(9\cos^2\Theta_4 - 1\right) + \sqrt{\frac{35\pi}{44}}i\left(\frac{3e}{R_5^6}\right)\sin^3\Theta_5\left(9\cos^2\Theta_5 - 1\right)\sin 3\Phi_5 \\
& - \frac{1}{4}\sqrt{\frac{35\pi}{11}}i\left(\frac{2e}{R_6^6}\right)\sin 3\Phi_6 - \cdots \\
B_{5-3} = & B_{53} \\
B_{55} = & \frac{3}{4}\sqrt{\frac{7\pi}{11}}i\left(\frac{-2e}{R_1^6}\right)\sin 5\Phi_1 - \frac{3}{8}\sqrt{\frac{7\pi}{11}}i\left(\frac{-2e}{R_2^6}\right) + \frac{3}{2}\sqrt{\frac{7\pi}{11}}i\left(\frac{-2e}{R_3^6}\right)\sin^5\Theta_3\sin 5\Phi_3 \\
& - \frac{3}{4}\sqrt{\frac{7\pi}{11}}i\left(\frac{2e}{R_4^6}\right)\sin^5\Theta_4 + \frac{3}{2}\sqrt{\frac{7\pi}{11}}i\left(\frac{3e}{R_5^6}\right)\sin^5\Theta_5\sin 5\Phi_5 + \frac{3}{4}\sqrt{\frac{7\pi}{11}}i\left(\frac{2e}{R_6^6}\right)\sin 5\Phi_6 + \cdots \\
B_{5-5} = & B_{55}
\end{aligned}
$$

$$
\begin{aligned}
B_{60} &= -\frac{5}{4}\sqrt{\frac{\pi}{13}}\left(\frac{-2e}{R_1^7}\right) - \frac{5}{8}\sqrt{\frac{\pi}{13}}\left(\frac{-2e}{R_2^7}\right) \\
&+ \frac{1}{2}\sqrt{\frac{\pi}{13}}\left(\frac{-2e}{R_3^7}\right)\left(231\cos^6\Theta_3 - 315\cos^4\Theta_3 + 105\cos^2\Theta_3 - 5\right) \\
&+ \frac{1}{4}\sqrt{\frac{\pi}{13}}\left(\frac{2e}{R_4^7}\right)\left(231\cos^6\Theta_4 - 315\cos^4\Theta_4 + 105\cos^2\Theta_4 - 5\right) \\
&+ \frac{1}{2}\sqrt{\frac{\pi}{13}}\left(\frac{3e}{R_5^7}\right)\left(231\cos^6\Theta_5 - 315\cos^4\Theta_5 + 105\cos^2\Theta_5 - 5\right) \\
&- \frac{5}{4}\sqrt{\frac{\pi}{13}}\left(\frac{2e}{R_6^7}\right) + 4\sqrt{\frac{\pi}{13}}\left(\frac{3e}{R_7^7}\right) + \cdots \\
B_{62} &= \frac{1}{8}\sqrt{\frac{105\pi}{13}}\left(\frac{-2e}{R_1^7}\right)\cos 2\Phi_1 - \frac{1}{16}\sqrt{\frac{105\pi}{13}}\left(\frac{-2e}{R_2^7}\right) \\
&+ \frac{1}{4}\sqrt{\frac{105\pi}{13}}\left(\frac{-2e}{R_3^7}\right)\sin^2\Theta_3\left(33\cos^4\Theta_3 - 18\cos^2\Theta_3 + 1\right)\cos 2\Phi_3 \\
&- \frac{1}{8}\sqrt{\frac{105\pi}{13}}\left(\frac{2e}{R_4^7}\right)\sin^2\Theta_4\left(33\cos^4\Theta_4 - 18\cos^2\Theta_4 + 1\right) \\
&+ \frac{1}{4}\sqrt{\frac{105\pi}{13}}\left(\frac{3e}{R_5^7}\right)\sin^2\Theta_5\left(33\cos^4\Theta_5 - 18\cos^2\Theta_5 + 1\right)\cos 2\Phi_5 \\
&+ \frac{1}{8}\sqrt{\frac{105\pi}{13}}\left(\frac{2e}{R_6^7}\right)\cos 2\Phi_6 - \cdots \\
B_{6-2} &= B_{62} \\
B_{64} &= -\frac{3}{8}\sqrt{\frac{14\pi}{13}}\left(\frac{-2e}{R_1^7}\right)\cos 4\Phi_1 - \frac{3}{16}\sqrt{\frac{14\pi}{13}}\left(\frac{-2e}{R_2^7}\right) \\
&+ \frac{3}{4}\sqrt{\frac{14\pi}{13}}\left(\frac{-2e}{R_3^7}\right)\sin^4\Theta_3\left(11\cos^2\Theta_3 - 1\right)\cos 4\Phi_3 \\
&+ \frac{3}{8}\sqrt{\frac{14\pi}{13}}\left(\frac{2e}{R_4^7}\right)\sin^4\Theta_4\left(11\cos^2\Theta_4 - 1\right) \\
&+ \frac{3}{4}\sqrt{\frac{14\pi}{13}}\left(\frac{3e}{R_5^7}\right)\sin^4\Theta_5\left(11\cos^2\Theta_5 - 1\right)\cos 4\Phi_5 \\
&- \frac{3}{8}\sqrt{\frac{14\pi}{13}}\left(\frac{2e}{R_6^7}\right)\cos 4\Phi_6 + \cdots \\
B_{6-4} &= B_{64} \\
B_{66} &= \frac{1}{8}\sqrt{\frac{231\pi}{13}}\left(\frac{-2e}{R_1^7}\right)\cos 6\Phi_1 - \frac{1}{16}\sqrt{\frac{231\pi}{13}}\left(\frac{-2e}{R_2^7}\right) \\
&+ \frac{1}{4}\sqrt{\frac{231\pi}{13}}\left(\frac{-2e}{R_3^7}\right)\sin^6\Theta_3\cos 6\Phi_3 - \frac{1}{8}\sqrt{\frac{231\pi}{13}}\left(\frac{2e}{R_4^7}\right)\sin^6\Theta_4 \\
&+ \frac{1}{4}\sqrt{\frac{231\pi}{13}}\left(\frac{3e}{R_5^7}\right)\sin^6\Theta_5\cos 6\Phi_5 \\
&+ \frac{1}{8}\sqrt{\frac{231\pi}{13}}\left(\frac{2e}{R_6^7}\right)\cos 6\Phi_6 - \cdots \\
B_{6-6} &= B_{66} \quad etc.. \qquad (3.2)
\end{aligned}
$$

If we use (x, y, z) coordinates, $V(r, \theta, \varphi)$ given by eq. (3.1) is rewritten in the following form:

$$\begin{aligned} V(x,y,z) &= \bar{B}_{20}\left(3z^2 - r^2\right) + \bar{B}_{22}\left(x^2 - y^2\right) \\ &+ \bar{B}_{40}\left(35z^4 - 30r^2z^2 + 3r^4\right) + \bar{B}_{42}\left(7z^2 - r^2\right)\left(x^2 - y^2\right) + \bar{B}_{44}\left(x^4 - 6x^2y^2 + y^4\right) \\ &+ \bar{B}_{60}\left(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6\right) + \bar{B}_{62}\left(33z^4 - 18z^2r^2 + r^4\right)\left(x^2 - y^2\right) \\ &+ \bar{B}_{64}\left(11z^2 - r^2\right)\left(x^4 - 6x^2y^2 + y^4\right) + \bar{B}_{66}\left(x^6 - 15x^4y^2 + 15x^2y^4 - y^6\right), \end{aligned} \tag{3.3}$$

where the terms expressed by odd functions with respect to x,y,z are omitted, because these terms are ineffective for orbital level splitting of Nd^{3+}. $\bar{B}_{20}$ etc. are proportional to

$$\bar{B}_{20} = \sqrt{\frac{5}{16\pi}} B_{20} \quad etc.. \tag{3.4}$$

The free Nd^{3+} ion has three 4f electrons and the lowest multiplet is given by $^4I_{9/2}$ ($J = 9/2$, L=6, $S = 3/2$). The interaction Hamiltonian between three f-electrons and the crystalline electric field is expressed as $\mathcal{H}_{crys}$ = -e $\sum_{i=1,2,3} V(x_i, y_i, z_i)$ (e>0). According to the operator equivalents method [6], we can rewrite $\sum_i V(x_i, y_i, z_i)$ in the form expressed by the total angular momentum operator $\boldsymbol{J}$. Then $\mathcal{H}_{crys}$ is obtained in the following form:

$$\begin{aligned} \mathcal{H}_{crys} = -e\Bigg[&\alpha\left\langle r^2\right\rangle\left\{\bar{B}_{20}\left(3J_z^2 - J(J+1)\right) + \frac{1}{2}\bar{B}_{22}\left(J_+^2 + J_-^2\right)\right\} \\ &+ \beta\left\langle r^4\right\rangle\Big\{\bar{B}_{40}\left(35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2\right) \\ &\quad + \frac{1}{4}\bar{B}_{42}\left(\left(J_+^2 + J_-^2\right)\left(7J_z^2 - J(J+1) - 5\right) + \left(7J_z^2 - J(J+1) - 5\right)\left(J_+^2 + J_-^2\right)\right) \\ &\quad + \frac{1}{2}\bar{B}_{44}\left(J_+^4 + J_-^4\right)\Big\} \\ &+ \gamma\left\langle r^6\right\rangle\Big\{\bar{B}_{60}\big(231J_z^6 - \left(315J(J+1) - 735\right)J_z^4 + \left(105J^2(J+1)^2 - 525J(J+1) + 294\right)J_z^2 \\ &\qquad - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)\big) \\ &\quad + \frac{1}{4}\bar{B}_{62}\big(33J_z^4 - \left(18J(J+1) + 123\right)J_z^2 + J^2(J+1)^2 + 10J(J+1) + 102\big)\left(J_+^2 + J_-^2\right) \\ &\qquad + \left(J_+^2 + J_-^2\right)\left(33J_z^4 - \left(18J(J+1) + 123\right)J_z^2 + J^2(J+1)^2 + 10J(J+1) + 102\right) \\ &\quad + \frac{1}{4}\bar{B}_{64}\left(\left(J_+^4 + J_-^4\right)\left(11J_z^2 - J(J+1) - 38\right) + \left(11J_z^2 - J(J+1) - 38\right)\left(J_+^4 + J_-^4\right)\right) \\ &\quad + \frac{1}{2}\bar{B}_{66}\left(J_+^6 + J_-^6\right)\Big\}\Bigg], \end{aligned} \tag{3.5}$$

where $\alpha = -\frac{7}{11^2 \cdot 3^2}$, $\beta = -\frac{2^3 \cdot 17}{13 \cdot 11^3 \cdot 3^3}$, $\gamma = -\frac{19 \cdot 17 \cdot 5}{13^2 \cdot 11^3 \cdot 7 \cdot 3^3}$. $\mathcal{H}_{crys}$ given by eq. (3.5) represents the anisotropy Hamiltonian for $\boldsymbol{J}$. Therefore on the basis of this Hamiltonian we can discuss the easy direction of the magnetic moment of Nd^{3+} which is given by $-g_J\mu_B\boldsymbol{J}$. For simplicity, if we consider the second order terms of $\boldsymbol{J}$, the easy direction of the magnetic moment is parallel to the y-axis (b-axis), because the coefficients of $(3J_z^2 - J(J+1))$ term and $(J_x^2 - J_y^2)$ term are positive. This result is consistent with the observed one by the neutron diffraction experiment. The energy of the ten-fold degeneracy of J-state is split by $\mathcal{H}_{crys}$. The crystalline electric fields arising from the 1st n.n. to the 35th neighbor are taken into consideration. We have calcutated eigenvalues and eigenfunctions of $\mathcal{H}_{crys}$ by using $< r^2 >$=2.04a.u., $< r^4 >$=6.27a.u. and $< r^6 >$=26.96a.u.. These are calculated by the use of Slater's semiempirical function for the 4f radial function of Nd^{3+} ion. The ground state is doubly degenerated and found to be

$$\begin{aligned} \psi_g &= a\psi_{\frac{9}{2}\frac{9}{2}} + b\psi_{\frac{9}{2}\frac{5}{2}} + c\psi_{\frac{9}{2}\frac{1}{2}} + d\psi_{\frac{9}{2}-\frac{3}{2}} + e\psi_{\frac{9}{2}-\frac{7}{2}} \\ \psi_g' &= e\psi_{\frac{9}{2}\frac{7}{2}} + d\psi_{\frac{9}{2}\frac{3}{2}} + c\psi_{\frac{9}{2}-\frac{1}{2}} + b\psi_{\frac{9}{2}-\frac{5}{2}} + a\psi_{\frac{9}{2}-\frac{9}{2}}. \end{aligned} \tag{3.6}$$

The wave functions of the five excited doublets have the same forms with those of the ground doublet. The coefficients a, b, $\cdots$, e are calculated as shown in Table 1.

In order to study which direction is the easy direction of the magnetic moment of Nd^{3+} in Nd_2BaNiO_5,

Table 1: Coefficients of the linear combination of $\Psi_{\frac{9}{2}\frac{9}{2}}, \Psi_{\frac{9}{2}\frac{7}{2}}$ etc. for the ground and excited states

	a	b	c	d	e
ground state	-0.0361	-0.1402	0.8524	-0.4987	-0.0615
1st excited state	-0.0930	-0.5443	0.3471	0.7572	-0.0346
2rd excited state	0.1478	0.8003	0.3694	0.4165	-0.1668
3rd excited state	0.0190	0.1079	0.1282	0.0661	0.9835
4th excited state	0.9838	-0.1789	0.0061	-0.0106	0.0005

we have first calculated the Zeeman splitting of the doubly degenerated ground state ψ_g and ψ'_g, and then magnetic susceptibility tensor $\chi_{\mu\nu}(\mu,\nu = x,y,z)$, where μ denotes the direction of the applied field and ν denotes the direction of the magnetic moment induced by the applied field. The calculated results are as follows:$\chi_{\mu\nu}$ becomes diagonal tensor and χ_{yy} is the largest compared with χ_{xx},χ_{zz}. Therefore, the easy direction of the magnetic moment of Nd is parallel to the y-axis, namely parallel to the c-axis. This is consistent with the observed result [2].

4 Conclusion

The single-ion type magnetic anisotropy of Ni^{2+} and Nd^{3+} ions of Nd_2BaNiO_5 caused by the crystalline electric field has been studied on the basis of the point charge model. For Ni^{2+} ion the easy direction of the magnetic moment is obtained to be parallel to the a-axis. This result is inconsistent with the observed one which is tilted from the a-axis toward the c-axis by the angle $\sim 55°$. To determine the easy direction of Ni moment a coupling between Ni and Nd moments should be taken into consideration. For Nd^{3+} ion we have succeeded in explaining the observed easy direction of Nd moment, which is parallel to the c-axis, by the single-ion type anistropy caused by the crystalline electric field.

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