

Article

Origin of Multiferroism of β -NaFeO₂

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Abstract: The multiferroic β -NaFeO₂ is theoretically investigated for the first time using a microscopic model and Green's function technique. A small room-temperature ferromagnetism is observed, which could be explained by canting of the antiferromagnetic sublattices. The ferromagnetic behaviour can be applied to applications in spintronic devices. We have investigated the temperature and magnetic field dependence of the spontaneous polarization P_s , as calculated from the transverse Ising model and the spin-assisted polarization ΔP due to magnetostriction and antisymmetric Dzyaloshinsky–Moriya interactions. The influence of external magnetic fields along the y and z axis is discussed. This is indirect evidence for the multiferroic behaviour of NaFeO₂. The temperature dependence of the relative dielectric permittivity is calculated.

Keywords: β -NaFeO₂; magnetization; polarization; relative dielectric permittivity; microscopic model



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1. Introduction

Materials that are both ferroelectric and magnetic—multiferroics—are rare in nature. Most multiferroic materials have simultaneous magnetic and ferroelectric orders at low temperatures. However, for their applications, the materials have to show ferroelectricity and ferromagnetism at room temperature. An example of a room-temperature multiferroic is β -NaFeO₂ (β -NFO), which shows a weak ferromagnetism (WFM) with a Curie temperature $T_C^{FM} \sim 723$ K [1,2]. This makes it a potentially promising material for applications in spintronic devices. The origin of WFM of β -NFO can be attributed to the presence of the Dzyaloshinsky–Moriya (DM) interactions in this compound. NFO can crystallize in different phases— α , β , γ : the first exists at low, the second at middle, and the third at high temperatures [3]. Only the α and β phases show ferroelectricity [1,4]. The γ phase is paraelectric [1]. The ferroelectric phase transition temperature T_C^{FE} of β -NFO is found at around 1373 K [1], which is much higher than its T_C^{FM} of 723 K. The recently magnetic properties of β -NFO nanoparticles are reported [5,6], which makes them applicable to the treatment of cancer via hyperthermia [7,8].

Unfortunately, there are no theoretical works to explain the multiferroicity of β -NFO. The main aim of this study is to observe the magnetoelectric effect in β -NFO using a microscopic model.

2. The Model

β -NFO crystallizes in a non-centrosymmetric orthorhombic structure Pn2₁a (see Figure 1) with lattice parameters $a = 5.6793$ Å, $b = 7.1243$ Å and $c = 5.3784$ Å [1]. The Fe³⁺ ions form a monoclinic lattice, where each magnetic ion has four nearest neighbors. The basic magnetic interaction is a super-exchange one Fe–O–Fe with an angle 113°–126° [2], which is not optimal for antiferromagnetic ordering. Neutronographic studies have shown that the magnetic moments of Fe³⁺ are arranged in a G-type antiferromagnetic structure along

the $b(y)$ axis with a phase transition temperature of $T_C^{FM} = 723$ K [1]. Magnetic measurements indicate the presence of a weak ferromagnetism with a spontaneous magnetic value of about $5.10^{-4} \mu_B/\text{cell}$ at room temperature with a deviation from the antiferromagnetic arrangement of 0.003° [1]. This behavior is a consequence of the presence of an antisymmetric DM exchange interaction. For symmetric reasons, it is clear that if the antiferromagnetic order is along the $b(y)$ axis, the appearance of the WFM is along the $c(z)$ axis as the DM vector has the form $\mathbf{D} = \mathbf{d}(\pm 1; 0; \pm 1)$. The sign and direction of the DM vector provides the relationship between the coordinates of the Fe ions in the elementary cell for each Fe-O-Fe bond [9]. Following the peculiarities of the crystalline structure, it is clear that the symmetric operators n and a do not impose any restriction on the polarization vector. The operator 2_1 (determining a rotation of 180° around the $b(y)$ axis) changes the atomic positions from (x, y, z) in $(-x, y, -z)$. This means that the polarization will only have a component along the $b(y)$ axis [10].

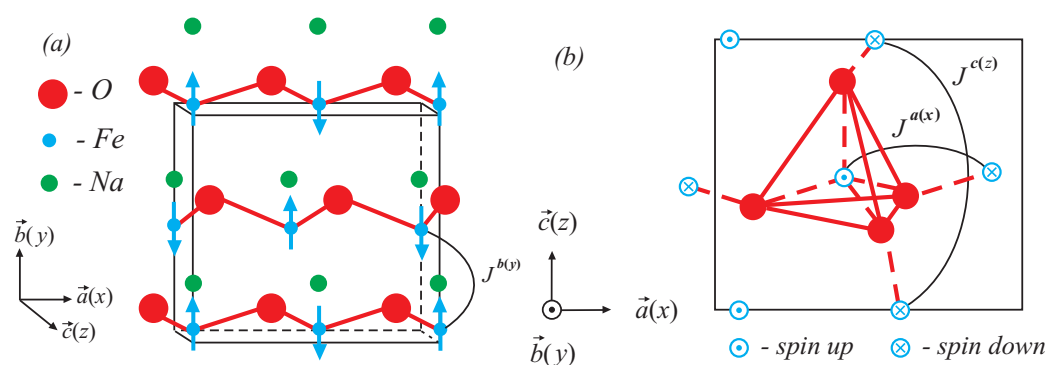


Figure 1. Scheme of the structure (a) and the magnetic interactions (b) of β -NFO.

The magnetic properties of β -NFO are described by a modified Heisenberg Hamiltonian H_m :

$$H_m = - \sum_{ij} \frac{1}{2} J_{ij}^z S_i^z S_j^z - \sum_{ij} \frac{1}{2} J_{ij}^x S_i^x S_j^x - \sum_{ij} \frac{1}{2} J_{ij}^y S_i^y S_j^y - \sum_{ij} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) - \sum_i K_i (S_i^y)^2 - g \mu_B \mathbf{h} \cdot \sum_i \mathbf{S}_i, \quad (1)$$

where \mathbf{S}_i is the Heisenberg spin operator of the Fe ion at the site i . J is the symmetric exchange interaction, K is the constant of the single-ion magnetic anisotropy, g is the gyromagnetic factor, and μ_B is the Bohr magneton. The first three terms in (1) describe the isotropic super-exchange interactions in the magnetic system as: $J^z > 0$ (see Figure 1b). This determines a ferromagnetic arrangement along the z axis, $J^x < 0$ (see Figure 1b) and $J^y < 0$ (see Figure 1a) determines an antiferromagnetic arrangement along the x and y axis, respectively. The fourth term includes the antisymmetric exchange DM interaction type and is responsible for the appearance of a weak ferromagnetism along the z axis. The fifth term in (1) defines the y -axis as the easy axis of the magnetization, i.e., $K_i > 0$. \mathbf{h} is an external magnetic field.

Since the crystal lattice of β -NFO is non-centrosymmetric, the spontaneous polarization appears at temperatures higher than T_C^{FE} . At temperatures above $T_C^{FE} = 1373$ K β -NFO is in a paraelectric state, where the lattice symmetry is tetragonal (the so-called γ -NFO). This means that, at $T_C^{FE} = 1373$ K, there is a structural phase transition from a paraelectric $P4_12_12$ centrosymmetric tetragonal phase into a non-centrosymmetric orthorhombic structure $Pn2_1a$ [1]. This is a phase transition of a displacive type. The polarization properties can

be described using the pseudo-spin formalism and the transverse Ising model (TIM) H_f , considering that, from a symmetrical point of view, the polarization is on the y axis:

$$H_f = -\Omega \sum_i B_i^z - \frac{1}{2} \sum_{ij} J'_{ij} B_i^y B_j^y. \quad (2)$$

The pseudo-spin operator B_i^y characterizes the two positions of the ferroelectric unit at the lattice point i . J'_{ij} denotes the nearest-neighbor pseudo-spin interaction. The dynamics of the ferroelectric part are realized by the first term with the flipping rate Ω and the operator B_i^z . The TIM was proposed by Blinc and de Gennes, describing order–disorder and displacive type ferroelectrics [11,12].

For β -NFO the Fe^{3+} ions are involved in the formation of the polar state through their displacements, together with those of the Na^+ ions relative to the oxygen matrix. Moreover, the same iron ions, due to super-exchange interactions, are responsible for the appearance of a G-type magnetic ordering and a weak ferromagnetism. This means that these compounds must be defined as multiferroics, in which an additional, spin-assisted polarization ΔP is also observed. From a theoretical perspective, the appearance of the magnetoelectric terms in the Hamiltonian H_{mf} is a consequence of the modulation of the symmetric and antisymmetric exchange interactions between the Fe^{3+} spins from the polar lattice displacements u_{ij} . Considering that $P_s = e^* \langle u \rangle$, where e^* is the Born charge, H_{mf} can be written as:

$$\begin{aligned} H_{mf} = & -\gamma_1 \sum_{ij} | \mathbf{P}_s | (\mathbf{S}_i \cdot \mathbf{S}_j) - \gamma_2 \sum_{ij} (\mathbf{P}_s)^2 (\mathbf{S}_i \cdot \mathbf{S}_j) \\ & - \lambda \sum_{ij} (\mathbf{P}_s \times \mathbf{e}_{ij}) \cdot (\mathbf{S}_i \times \mathbf{S}_j). \end{aligned} \quad (3)$$

γ_1 and λ are the first derivatives of the exchange interaction J and of the DM vector on the polar displacements u_{ij} , respectively, and γ_2 is the second derivative of J on u_{ij} . The terms in (3) are formally similar to the Peierls-type spin–phonon interactions. Note that P_s is responsible for the change in the hybridization of the magnetic Fe–O–Fe and Fe–O–O–Fe bonds, i.e., under T_C^{FM} , the magnetic arrangement is influenced by the spontaneous polarization.

Finally, the total Hamiltonian for the description of the multiferroic properties of β -NFO takes the form:

$$H = H_m + H_f + H_{mf}. \quad (4)$$

Comparing the third term in Equation (3) with the fourth one in (1), it can be concluded that the spontaneous polarization induces a DM interaction with a vector $\mathbf{D}_{ij}^{ind} = \lambda (\mathbf{P}_s \times \mathbf{e}_{ij})$. This leads to an effective temperature-dependent DM vector:

$$\mathbf{D}_{ij}^{eff} = \mathbf{D}_{ij} + \mathbf{D}_{ij}^{ind}, \quad (5)$$

which, below T_C^{FM} increases, with decreases in temperature.

Analogically, the first and second terms in Equation (3) mean that the isotropic exchange interaction J is also temperature-dependent:

$$J^{eff} = J + \gamma_1 | P_s | + \gamma_2 | P_s |^2. \quad (6)$$

Qualitatively, Equations (5) and (6) define a kind of a feedback connection between the two subsystems. The spontaneous polarization changes the nature of the symmetric and antisymmetric exchange interactions. However, below the ferromagnetic phase transition temperature T_C^{FM} , due to the magnetic ordering, the spontaneous polarization will be changed and “controlled” through renormalization of the pseudo-spin interaction and the tunneling rate by applying a magnetic field and the appearance of a spin-assisted additive polarization ΔP_{tot} .

Let us emphasize that a strong spin–phonon interaction is reported in ABO₂ compounds (A = Cu, Ag, Na, Li and B = Fe, Cr) [13]. Therefore, a further polarization may be a consequence of magnetostriction (MS) effects:

$$\Delta P_{ss} \sim \sum_{ij} \langle (\mathbf{S}_i \cdot \mathbf{S}_j) \rangle \quad (7)$$

or (and) inverse DM mechanism [14]:

$$(\Delta P_{IDM})^d \sim \sum_{ij} \langle \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j) \rangle^d, \quad d = (x, y, z), \quad (8)$$

where d are the components of ΔP . The second mechanism is characteristic for compounds in which non-collinear magnetic structures (commensurate and non-commensurate spirals) are observed, and for crystals, which have a two fold axis perpendicular to \mathbf{e}_{ij} , or a mirror plane of symmetry containing \mathbf{e}_{ij} . In our opinion, this is not the case in β -NFO. As Kaplan et al. [10] have shown, in the absence of such elements of symmetry, an additional polarization resulting from the DM interaction will appear:

$$\Delta P_{as}^d \sim \sum_{ij} \langle (\mathbf{S}_i \times \mathbf{S}_j) \rangle^d, \quad d = (x, y, z). \quad (9)$$

Therefore the spin-assisted polarization is calculated from the following equation:

$$\Delta P_{tot} = \Delta P_{ss} + \Delta P_{as}. \quad (10)$$

From Equation (2), it can be seen that the ferroelectric ordered phase is characterized by non-zero mean values of $\langle B^y \rangle$ and $\langle B^z \rangle$. In order to obtain, below the ferroelectric phase-transition temperature T_C^{FE} , one order of parameter that determines spontaneous polarization, the coordinate system is rotated around the x axis at about an angle of θ , which is the angle locked between the direction of the pseudo-spin vector and the positive direction of the y -axis. θ is determined from the requirements of $\langle B^{z'} \rangle = 0$ in the new coordinate system:

$$\langle B_i^y \rangle = \frac{1}{2} \tanh \left(\frac{E_i}{2k_B T} \right) \cos \theta_i. \quad (11)$$

E_i is the pseudo-spin wave energy observed from the poles of the Green's function $G_{ij} = \langle \langle B_i^+; B_j^- \rangle \rangle$.

From the 3×3 matrix Green's function $g_{ij} = \langle \langle S_i^{+, -z}; S_j^{-, +z} \rangle \rangle$, the expression for the magnetization M_c is calculated as follows:

$$M_c = \frac{1}{N} \sum_i \langle S_i^z \rangle = \frac{1}{N} \sum_i \left[(S + 0.5) \coth \left(\frac{(S + 0.5)\omega_i}{k_B T} \right) - 0.5 \coth \left(\frac{0.5\omega_i}{k_B T} \right) \right], \quad (12)$$

where ω_i is the spin-wave energy.

For the spin-assisted additive polarizations, we have observed:

$$\Delta P_{ss} \sim \frac{2}{N} \sum_{ij} \left(\langle S_i^- S_j^+ \rangle + \langle S_i^z S_j^z \rangle \right), \quad (13)$$

$$\Delta P_{as} \sim \frac{1}{2N} \sum_{ij} \left(\langle S_i^z S_j^- \rangle + \langle S_i^z S_j^+ \rangle \right). \quad (14)$$

The correlation functions are obtained using the Spectral theorem.

3. Numerical Results and Discussion

For the numerical calculations of the properties of β -NFO, we will use the following model parameters for the magnetic subsystem: $J^x = -61.94$ K, $J^z = 17.27$ K, $J^y = -9.84$ K, $d = 0.26$ K, $K = 0.034$ K, $S = 5/2$, $T_C^{FM} = 723$ K. For the ferroelectric subsystem, we use the following: $J' = 1472.28$ K, $\Omega = 16.47$ K, $s = 1/2$, $T_C^{FE} = 1373$ K.

We will provide a short description of the calculation of some model parameters. From Figure 1b, it can be seen that, along the a axis, the spins are ordered antiferromagnetically, with type Fe-O-Fe. Along the c axis, the spins are ordered ferromagnetically, with type Fe-O-O-Fe (next nearest neighbors) (Figure 1b), which leads to a smaller interaction compared to that along the a axis. The exchange interaction J^x along the x axis in the ac plane is approximately observed from the expression in the mean field approximation $J^x = 3k_B T_C^{FM} / (zS(S+1))$, where k_B is the Boltzmann constant, $z = 4$ is the number of nearest neighbors, $S = 5/2$ is the spin value, and T_C^{FM} is the magnetic critical temperature. The above expression for J^x determines the magnitude of the exchange interaction value while the magnetic configuration is its sign. There is an antiferromagnetic arrangement along the x -axis (see Figure 1b). This means that the sign of J^x is negative. Finally, we find that $J^x = -61.94$ K. It must be noted that the units for all exchange interactions are shown in Kelvin [K] as $1J = 0.724 \times 10^{23}$ K [15]. J^z along the z axis is calculated, considering the dependence of the magnetic exchange interaction constant on the distance r between two neighbouring spins, $J \sim 1/r^2$, as follows: $J^z \sim -(a/2c)^2 J^x = 17.27$ K. Using the same assumption, we observe for $J^y \sim (a/2b)^2 J^x = -9.84$ K. Following [16], we can observe the DM constant from the relation between the canting angle τ and the value of the DM vector D : $\sin \tau = -D/(2J^x) = -d/(\sqrt{2}J^x)$. With $\tau = 0.003^\circ$ [1], i.e., $\sin \tau \sim \tau$, we can observe $d = -\sqrt{2}\tau J^x = 0.26$ K. The model parameters for the ferroelectric subsystem J' and Ω are calculated from the following expressions: $2\Omega/J' = \tanh(0.5\beta_c\Omega)$, $\beta_c = 1/(k_B T_C^{FE})$, below T_C^{FE} and $2\Omega \approx E_i$ with $E_i \approx 40$ – 45 K (the energies of the ferroelectric system assumed within our model) at very high temperatures [11].

Firstly, we will study the magnetic field and temperature dependence of the magnetization of β -NFO. The results are presented in Figure 2. We observe that β -NFO exhibits a WFM, a magnetization M_c along the c axis, which is in agreement with the experimental data of Viret et al. [1] and Watanabe et al. [2]. The WFM decreases with increasing temperature and vanishes for a magnetic field $h = 0$ at a critical temperature $T_C^{FM} = 723$ K. We also investigated the influence of an external magnetic field h in the c direction on the magnetization M_c . The hysteresis is shown as being inset in Figure 2. It can be seen that this shows a typical ferromagnetic behavior. This behavior could be due to the spin-canted Fe moments, to the competition between antiferromagnetic super-exchange and ferromagnetic interactions, or to the antisymmetric DM interactions. It should be mentioned that the latter could also depend on the coupling between local spins and electrical polarization. Let us emphasize that the DM interaction, which is the main origin of the WFM, leads to its increase. For $D = 0$, there is not a WFM, the magnetization M_c is zero.

Figure 3 shows the temperature dependence of the spontaneous polarization P_s along the b axis, which vanishes at $T_C^{FE} = 1373$ K, a phase transformation from the orthorhombic to tetragonal phase. The hysteresis of P_s is reported by Viret et al. [1]. In P_s , there are two contributions: curve 2 describes the spontaneous polarization observed from the TIM P_s^{TIM} , whereas curve 1 describes the behavior of P_s , also considering the ME interactions in β -NFO. At $T_C^{FM} = 723$ K, a “kink” is observed (see curve 1). The additional contribution in P_s is due to the appearance under T_C^{FM} of an additional spin-dependent polarization ΔP_{tot} (curve 3), which is due to the MS and the antisymmetric DM interaction. In the “inset”, the temperature dependence of the relative dielectric permittivity ϵ is presented, where a peak is observed at the magnetic-phase transition temperature T_C^{FM} . This is evidence of the presence of ME interactions in β -NFO. The appearance of the additional polarization ΔP_{tot} , which is spin-dependent, determines the possibility of controlling P_s in this compound within an external magnetic field h at room temperature.

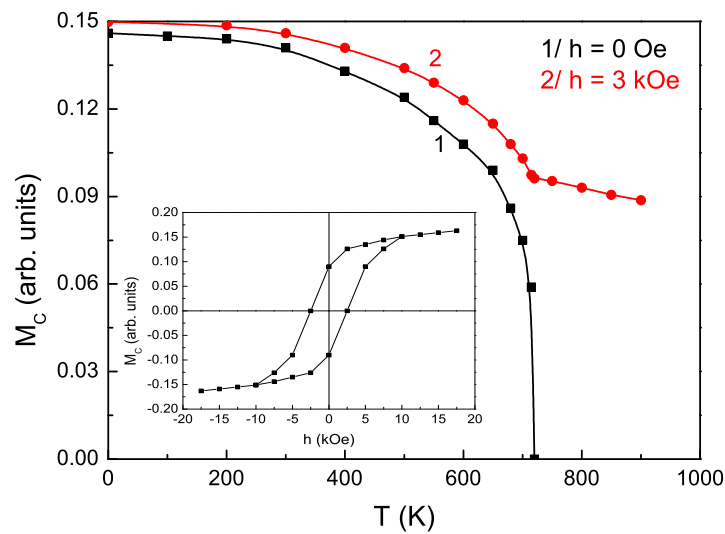


Figure 2. The temperature dependence of the magnetization M_C , of the WFM of β -NFO for different magnetic fields h : (1) 0, (2) 3 kOe. Inset: Hysteresis loop of the magnetization M_C for $T = 600$ K.

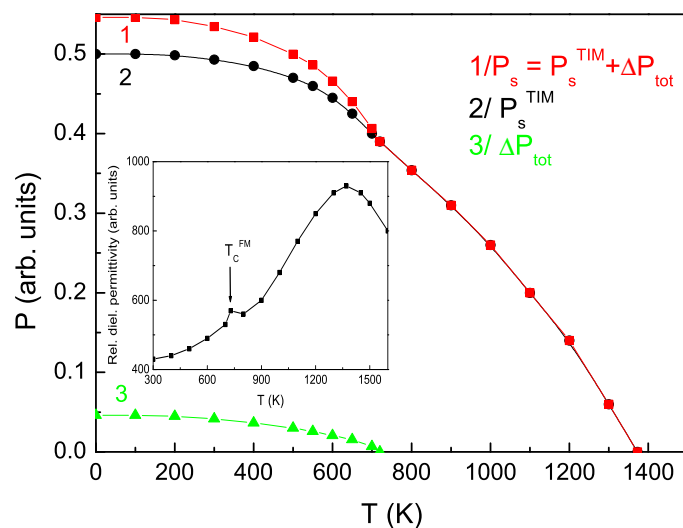


Figure 3. Temperature dependence of the spontaneous polarization P_s (curve 1) in β -NFO as a sum of P_s^{TIM} (curve 2), calculated from the transverse Ising model, and ΔP_{tot} (curve 3), observed considering the ME interactions. Inset: Temperature dependence of the relative dielectric permittivity ϵ with a kink at T_C^{FM} .

The relative dielectric permittivity ϵ is calculated from equation [17]:

$$((\Lambda/(\epsilon(\mathbf{k}, E) - 1))_{\alpha\beta} + \Lambda \frac{k_\alpha k_\beta}{k^2}) G^{\beta\gamma}(\mathbf{k}, E) = \delta_{\alpha\gamma}; \quad \Lambda = 4\pi Z^2/v, \quad (15)$$

where \mathbf{k} is wave vector, E is energy or frequency, the indices α, β, γ are the components of the related spins, δ is the delta function, Z is the electron charge and v is the volume. To study the relative dielectric permittivity $\epsilon(\mathbf{k}, E)$, we need the Green's function $G^{xx}(\mathbf{k}, E)$:

$$G^{xx}(\mathbf{k}, E) = \frac{2P_s(\epsilon_{11} - \epsilon_{12})}{E^2 - E_k^2 + 2iE\gamma_{11}}, \quad (16)$$

E_k and γ_{11} are the transverse pseudo-spin wave energy and its damping.

The contributions of each of the mechanisms to ΔP_{tot} are presented in the next Figure. From the temperature dependence of ΔP_{tot} (see Figure 4, curve 1), this can be seen to disappear at the magnetic-phase transition temperature T_C^{FM} . Curves 2 and 3 determine the contributions of the two mechanisms to the additional polarization, ΔP_{ss} and ΔP_{as} , due to the MS and the antisymmetric DM interaction, respectively. It is clear that the additional polarization associated with the MS (curve 2) prevails over that due to the DM-related interaction (curve 3).

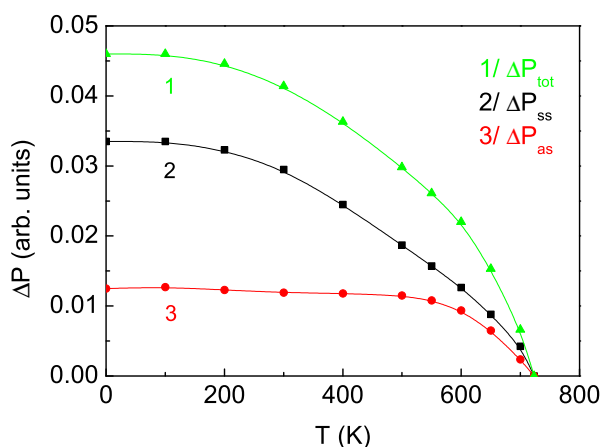


Figure 4. Temperature dependence of the total spin-assisted polarization ΔP_{tot} curve (1) due to the contributions of the MS ΔP_{ss} (curve 2) and the antisymmetric DM magnetic interaction ΔP_{as} (curve 3).

Figure 5 presents the dependence of the spin-dependent polarization ΔP_{tot} on the DM vector D , whereas the inset shows the dependence on the magnetic anisotropy constant K for different temperature values (curves 1 and 2). As D increases, the value of the additional polarization increases, while as K grows, it decreases. These results are expected because the antisymmetric magnetic interaction (the intensity of which depends on the size of the DM vector D) determines the presence of a magnetoelectric (ME) mechanism (see the third term in Equation (3)) for the occurrence of the additional polarisation ΔP_{as} (see Equation (9)). As D grows, the “canting” angle and WFM will increase, leading to an increase in the contribution of ΔP_{as} . However, enhancing K will lead to stabilization of the antiferromagnetic G-structure, a decrease in the “canting” angle, and the WFM. The contribution of ΔP_{as} due to the antisymmetric DM interaction decreases; therefore, ΔP_{tot} also decreases.

Figure 6 shows the dependence of the additional spin-dependent polarisation as a function of an external magnetic field applied in the y direction at a fixed temperature below T_C^{FM} . As the field increases, the influence of the spin-dependent polarization increases (curve 1). However, the components of ΔP_{tot} with the field are different. Using the MS mechanism, ΔP_{ss} increases as the magnetic field increases (curve 2), while ΔP_{as} decreases (curve 3). In contrast, when the applied magnetic field is along the z axis (see Figure 7) the influence of the spin-assisted polarization decreases when the magnetic field increases (curve 1), as ΔP_{ss} decreases with the field (curve 2), whereas ΔP_{as} increases (curve 3). This means that there is competition between the two mechanisms and, when the field increases, depending on its direction, the two mechanisms will always have different behaviors (if one mechanism leads to an increase in the polarization P_s , the other will lead to its reduction). As a result, in an external magnetic field applied in the y direction, the spontaneous polarization P_s of the system will increase as the field increases, while, if h is in the z direction, P_s will decrease. The dynamics in the change in the spontaneous polarization is mainly determined by the MS mechanism (this is more sensitive to changes in the value of the field compared to those due to DM interactions).

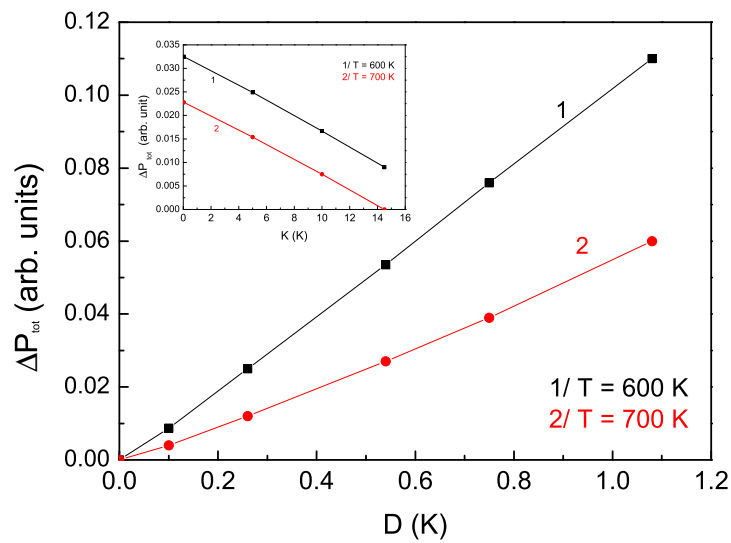


Figure 5. Dependence of the total spin-assisted polarization ΔP_{tot} on the DM vector D and in the inset on the anisotropy constant K for different temperatures $T = 600$ (1) and 700 K (2).

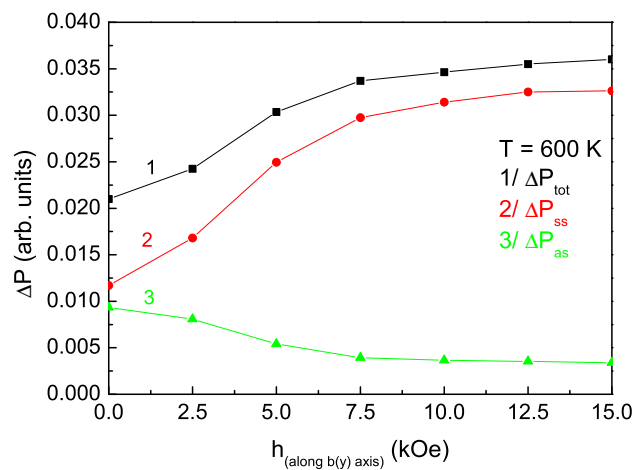


Figure 6. Dependence of the spin-assisted polarization on the magnetic field along the y axis of β -NFO for $T = 600$ K: (1) ΔP_{tot} , (2) ΔP_{ss} , (3) ΔP_{as} .

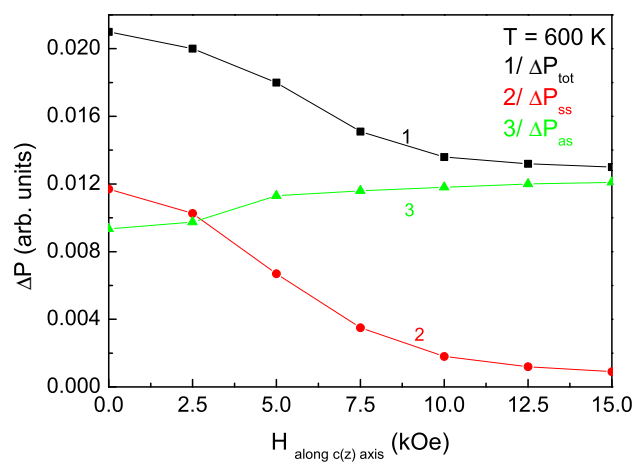


Figure 7. Dependence of the spin-assisted polarization on the magnetic field along the z axis of β -NFO for $T = 600$ K: (1) ΔP_{tot} , (2) ΔP_{ss} , (3) ΔP_{as} .

From a theoretical perspective, the reason for the dependence of the spontaneous polarization on the direction and size of the field below T_C^{FM} is, in our opinion, due to the influence of the ME mechanisms on the basic microscopic parameters of the pseudo-spin system, namely, on the flipping rate Ω and pseudo-spin interchange interaction J' . Below the magnetic phase transition temperature, they are renormalized and spin-dependent. Theoretical calculations lead to the following expressions: $J_{ij}'^{eff} = J_{ij}' + 2\gamma_2(\langle S_i^- S_j^+ \rangle + \langle S_i^z S_j^z \rangle)$ and $\Omega_{eff} = \Omega + 2[d_{eff} + \lambda \sum_{ij}(\langle S_i^z S_j^- \rangle + \langle S_i^z S_j^+ \rangle)]$ where $d_{eff} = d + \lambda |\mathbf{P}_s|$. From these expressions, it is clear that the ME interaction due to the MS renormalizes the pseudo-spin exchange interaction J_{ij}' , whereas the ME interaction connected with the DM interaction renormalizes the flipping rate Ω . The numerical calculations show that, with a constant temperature and increasing magnetic field along the y axis, Ω_{eff} increases, which, according to the TIM, will decrease P_s , i.e., the antisymmetric ME interaction $-\lambda \sum_{ij}(\mathbf{P}_s \times \mathbf{e}_{ij}) \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ destabilizes the ferroelectric phase. Under the same conditions, the calculations show that $J_{ij}'^{eff}$ would increase, which, according to the TIM, means that P_s would also increase, i.e., the ME interaction connected with the MS $-\gamma_1 \sum_{ij} |\mathbf{P}_s| (\mathbf{S}_i \cdot \mathbf{S}_j) - \gamma_2 \sum_{ij} (\mathbf{P}_s)^2 (\mathbf{S}_i \cdot \mathbf{S}_j)$ stabilizes the ferroelectric phase. However, for h in the direction of the z axis at a constant temperature, the numerical calculations indicate that Ω_{eff} decreases with increasing h , which means that following the TIM, P_s would increase, i.e., the antisymmetric ME interaction will stabilize the ferroelectric phase. Under the same conditions, the calculations show that $J_{ij}'^{eff}$ would decrease, which, within the TIM, means that P_s would also be reduced, i.e., the ME interaction associated with the MS would destabilize the ferroelectric phase. The magnetic field dependence of the polarization is evidence for the multiferroic behavior of β -NFO. Unfortunately, to our knowledge, there are no experimental data for the temperature and magnetic field dependence of the polarization $P(T, h)$.

4. Conclusions

In conclusion, we have theoretically investigated the multiferroic properties of β -NFO for the first time. We have observed a small ferromagnetism along the c axis, which makes β -NFO a promising material for applications in spintronic devices.

Moreover, we have calculated the spontaneous polarization P_s along the b axis, as well as the spin-assisted polarization ΔP , due to the ME interactions, including the MS and the DM interaction. The temperature dependence of the relative dielectric permittivity is also observed, which shows a kink at T_C^{FM} .

The study presents interesting results regarding the influence of an external magnetic field along the y and z axis on ΔP . The latter is evidence for the MF behaviour of β -NFO. Further experimental and theoretical studies are clearly needed to explain the multiferroic behaviour of β -NFO.

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Conflicts of Interest: The authors declare no conflict of interest.

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