Evidence for differentiation in the iron-helicoidal-chain in GdFe$_3$(BO$_3$)$_4$

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We report on a single-crystal X-ray structure study of GdFe$_3$(BO$_3$)$_4$ at room temperature and at $T=90$ K. At room temperature GdFe$_3$(BO$_3$)$_4$ crystallizes in a trigonal space group $R32$ (No. 155), the same as found for other members of iron-borate family RFe$_3$(BO$_3$)$_4$. At 90 K the structure of GdFe$_3$(BO$_3$)$_4$ transforms to the space group $P3_121$ (No. 152). The low-temperature structural determination gives new insight into the weakly first-order structural phase transition at 156 K and into the related Raman phonon anomalies. The presence of two inequivalent iron chains in the low temperature structure provides a new perspective on the interpretation of the low-temperature magnetic properties.

I. INTRODUCTION

The family of borates RM$_3$(BO$_3$)$_4$ with a rare earth (RE) or yttrium as R and Al, Ga, Fe, or Sc as M crystallize in the huffite, CaMg$_3$(CO$_3$)$_4$, structure type with space group $R32$. The interest in this family of crystals arises both from a fundamental point of view and from already realized and proposed applications. Crystals of YAl$_3$(BO$_3$)$_4$ and GdAl$_3$(BO$_3$)$_4$ doped with Nd were widely studied during recent years and have been used in optical devices, such as self-frequency doubling and self-frequency summing lasers (see, e.g., Ref. and references therein). Concentrated NdAl$_3$(BO$_3$)$_4$ crystals are efficient media for minilasers. Apart from the interesting optical properties arising chiefly from the lack of inversion symmetry, the ‘sub-family’ of RFe$_3$(BO$_3$)$_4$ also attracts considerable attention due to their structure peculiarities. The presence of magnetic order at temperatures less then 37 K was attributed to magnetic Fe-Fe or Fe-O-Fe interactions inside quasi one-dimensional (1D) iron chains. Recent works focusing on low temperature magnetism in GdFe$_3$(BO$_3$)$_4$, revealed two magnetic phase transitions. The second-order magnetic ordering phase transition at $T_N=37$ K (antiferromagnetic ordering of Fe atoms) is followed by a first-order spin-reorientation phase transition at $T_{N1}=10$ K. Additionally specific heat and Raman measurements on single crystals of GdFe$_3$(BO$_3$)$_4$ revealed a weakly first-order structural phase transition at $T_a=156$ K. This structural phase transition is observed in almost all members of the RE ferro-borates family. Recently, Hinatsu et al. have shown that DyFe$_3$(BO$_3$)$_4$ undergoes such structural phase transition at 340 K, by measuring the temperature dependence of the lattice parameters on powder samples. Here too, a peak in the specific heat was observed at this temperature. Similar peaks in specific heat vs temperature dependence were found for other heavy RE (R= Eu-Ho, Gd, Tb) ferroborates. These peaks were ascribed to structural phase transitions. The transition temperatures $T_a$ were found to depend linearly on the ionic radius of the RE. To date, there are no single crystal data available nor has the low-temperature (LT) space group been determined.

The high temperature (HT) $R32$ structure of powder RFe$_3$(BO$_3$)$_4$ compounds was first determined in Ref. for R = La, Nd, Sm-Ho, and Y. X-ray experiments on single crystals with $R=$Nd$_{0.75}$Bi$_{0.25}$ and $R=$La, Nd, and Y$_{0.5}$Bi$_{0.5}$ confirmed this structure. Moreover, Raman measurements for LaFe$_3$(BO$_3$)$_4$ and GdFe$_3$(BO$_3$)$_4$ confirmed this structure. Furthermore, Raman measurements for $R$Fe$_3$(BO$_3$)$_4$ revealed a weakly first-order structural phase transition at $T_a=156$ K. This structural phase transition is observed in almost all members of the RE ferro-borates family. Recently, Hinatsu et al. have shown that DyFe$_3$(BO$_3$)$_4$ undergoes such structural phase transition at 340 K, by measuring the temperature dependence of the lattice parameters on powder samples. Here too, a peak in the specific heat was observed at this temperature. Similar peaks in specific heat vs temperature dependence were found for other heavy RE (R= Eu-Ho, Gd, Tb) ferroborates. These peaks were ascribed to structural phase transitions. The transition temperatures $T_a$ were found to depend linearly on the ionic radius of the RE. To date, there are no single crystal data available nor has the low-temperature (LT) space group been determined.

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II. EXPERIMENT AND RESULT OF STRUCTURE DETERMINATION

Crystals of GdFe$_3$(BO$_3$)$_4$ were grown using a K$_2$Mo$_3$O$_4$-based flux, as described in Ref. Big transparent single crystals of gadolinium iron borate were light green in color and had a good optical quality. A block-shaped crystal (‘broken-fragment’) with the dimensions of $0.22 \times 0.15 \times 0.11$ mm$^3$ was mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer. The crystal was cooled to 90(1) K using a Bruker KRYOFLEX. Intensity measurements were performed using graphite monochromated Mo-Kα radiation. Generator settings were
SMART was used for preliminary determination of the unit cell constants and data collection control. The intensities of reflections of a hemisphere were collected by a combination of 6 sets of exposures (frames). Each set had a different angle for the crystal and each exposure covered a range of $0.3^\circ$ in $\omega$. A total of 3600 frames were collected with an exposure time of 10.0 seconds per frame. The overall data collection time was 16 hours. Data integration and global cell refinement was performed with the program SAINT. The final unit cell was obtained from the xyz centroids of 4767 and 5439 reflections after integration for RT and 90 K, respectively. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption (an analytical absorption correction was applied), and reduced to $F_o^2$. The program suite SHELXTL was used for space group determination (XPREP).

![Diagram of GdFe$_3$(BO$_3$)$_4$](image)

**FIG. 1:** The structure of GdFe$_3$(BO$_3$)$_4$ in two different projection. The left panels (a) and (b) show the RT structure, and the right panels (c) and (d) show the structure at 90 K. The Fe atoms are arranged in chiral chains parallel to the c-axis. Different chains are separated by GdO$_6$ prisms and BO$_3$ groups. The unit cell outline for R32 is shifted by (1/3, 1/3, 0) for comparison with the LT P3$_1$21 structure.

At both temperatures of RT and 90 K the unit cell was identified as trigonal: reduced cell calculations did not indicate any higher metric lattice symmetry. Space groups R32 and P3$_1$21 were derived for RT and for 90 K, respectively, from the systematic extinctions and discriminated from other candidate space groups, which comply with the same extinctions conditions, during the structure determination process. Examination of the final atomic coordinates of the structure did not yield extra crystallographic or metric symmetry elements.

The polarity of the structure of the crystal actually chosen was determined by Flack's x-refinement; refinement resulted in a x value of 0.50(1), so ultimately an inversion twin is used in the refinement.

Crystal data and numerical details on data collection and refinement are given in Table I. Final fractional atomic coordinates, equivalent displacement parameters and anisotropic displacement parameters are given in Table II for data at RT and in Table III for the 90 K data.

### III. DISCUSSION OF THE STRUCTURE

After a brief introduction describing the main features of GdFe$_3$(BO$_3$)$_4$, we will focus on the difference between the RT and the 90 K (LT) structure. First, we will try to understand the consequences that the structural changes have on the interpretation of Raman spectra anomalies at the weak first-order phase transition reported in the literature. Second, we will give a new perspective for the interpretation of low temperature magnetic data.
TABLE I: Crystallographic parameters

| Parameter | Value |
|-----------|-------|
| Moity Formula | GdFe₃(BO₃)₄ |
| Crystal System | Trigonal |
| Space group | P3₁21, 152 |
| Unit cell (Å) | a = 9.5209(6), b = 7.5479(2), c = 5.9373(1) |
| Formula Weight (g mol⁻¹) | 560.04 |
| ρ (g/cm³) | 4.699 |
| μ (MoKα) | 9.5203(6) |
| F(000) electrons | 774 |
| Detector area resolution (pixels/mm) | 4096 |
| Data with criterion: | \(|F_o| > 4.0 \sigma(F_o)\) |
| Unique data | 755 |
| Total data | 4700 |
| Number of reflections | 755 |
| Number of refined parameters | 35 |
| Isotropic secondary-extinction coefficient, g | 0.0151 |
| Flack’s x | 0.50 |
| Final agreement factors: | 0.0374 |
| Room Temperature = 293(1) K T = 90(1) K |

TABLE II: Fractional atomic coordinates and Anisotropic Parameters at RT

| Atom | Wyckoff | Schoenflies | x | y | z | Ueq(Å) |
|------|---------|-------------|---|---|---|---------|
| Gd | 3a | D₃ | 0 | 0 | 0 | 0.00867(5) |
| Fe | 9d | C₂ | 0.21659(5) | 1/3 | 1/3 | 0.00654(9) |
| O₁ | 9e | C₂ | 0.1442(2) | x | 1/2 | 0.0083(3) |
| O₂ | 9e | C₂ | 0.4087(3) | x | 1/2 | 0.0132(5) |
| O₃ | 18f | C₁ | 0.2254(2) | 0.2125(2) | 0.1824(2) | 0.0095(3) |
| B₁ | 3b | D₃ | 0 | 0 | 0 | 0.0066(6) |
| B₂ | 9e | C₂ | 0.5526(3) | x | 1/2 | 0.0077(4) |

| Atom | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|------|------|------|------|------|------|------|
| Gd | 0.00888(8) | 0.00888(8) | 0.00825(9) | 0.00000(1) | 0.00000(1) | 0.00000(1) |
| Fe | 0.00591(12) | 0.00635(14) | 0.00750(18) | 0.00009(8) | 0.00000(4) | 0.00000(4) |
| O₁ | 0.00658(5) | 0.0058(5) | 0.00199(7) | 0.0014(3) | 0.0014(3) | 0.0011(6) |
| O₂ | 0.0076(6) | 0.0076(6) | 0.0182(11) | 0.0047(5) | 0.0047(5) | 0.0009(8) |
| O₃ | 0.00658(5) | 0.0112(5) | 0.0111(5) | 0.0025(5) | 0.0024(1) | 0.0000(4) |
| B₁ | 0.00589(9) | 0.0058(9) | 0.0081(4) | 0.00000(0) | 0.00000(0) | 0.00000(0) |
| B₂ | 0.0070(7) | 0.0070(7) | 0.0093(8) | 0.0007(4) | 0.0007(4) | 0.00036(11) |
TABLE III: Fractional atomic coordinates and Anisotropic Parameters at T=90 K

| Atom   | Wyckoff Schoenflies | x   | y   | z   | U_{eq}(\text{Å}) |
|--------|----------------------|-----|-----|-----|------------------|
| Gd     | 3 a C2               | -0.3342(1) | x   | 0   | 0.00406(4)       |
| Fe1    | 3 a C2               | 0.11536(5) | x   | 0   | 0.00360(6)       |
| Fe2    | 6 c C1              | -0.21420(6) | -0.54975(4) | 0.34154(2) | 0.00366(6)       |
| O1     | 3 b C2               | 0   | -0.07819(15) | 1/6 | 0.0072(3)        |
| O2     | 6 c C1              | -0.5832(2) | -0.2709(1) | 0.13774(12) | 0.00692(17)      |
| O3     | 6 c C1              | -0.21420(6) | -0.54975(4) | 0.34154(2) | 0.00366(6)       |
| O4     | 6 c C1              | -0.21420(6) | -0.54975(4) | 0.34154(2) | 0.00366(6)       |
| O5     | 6 c C1              | -0.21420(6) | -0.54975(4) | 0.34154(2) | 0.00366(6)       |
| O6     | 3 b C2               | 0.1877(2) | 0   | 5/6 | 0.0049(3)        |
| O7     | 6 c C1              | -0.5235(3) | -0.5381(1) | -0.18533(18) | 0.0056(2)       |
| B2a    | 6 c C1              | -0.4473(4) | -0.1201(-) | 0.15617(14) | 0.0053(3)       |
| B2b    | 3 b C2               | 0   | -0.2223(3) | 1/6 | 0.0049(4)        |
| B1     | 3 b C2               | 0.33204(14) | 0   | 5/6 | 0.0045(5)        |

nearly perpendicular to the C3 axis and the Fe atoms are arranged in helicoidal chains parallel to this axis. Different chains are connected by GdO6 and BO3 groups, where each individual BO3 and GdO6 group connects three chains. The distance between Fe atoms in the same chain (3.1669(4) Å) is shorter than the Fe-Fe distances for two nearest chains, that varies along the chain, 4.8308(5) Å, being the shortest one. The main exchange interaction between Fe3+ is therefore of quasi-1D nature.

TABLE IV: Symmetry position of BO3 groups, angle between the group and the c-axis and their flatness of them. The flatness is expressed as distance of the B atoms from the plane defined by the three oxygen ligands.

| Symmetry | Angle [deg.] | Flatness |
|----------|--------------|----------|
| Room Temperature | Low Temperature |
| B1 D3  | 90 | 0 | B1 C2 | 87.52(4) | 0.00009(1) |
| B2 C2 | 84.37(11) | 0 | B2a C1 | 81.89 | 0.00005(11) |
|         |       |   | B2b C2 | 83.55 | 0.0000(2) |

Upon lowering the temperature the GdFe3(BO3)4 crystal reduces the symmetry from R32 to P3121, in the trigonal system. Fig. 2 shows the coordination polyhedra (GdO6, FeO6, and BO3) for two different structures R32 and P3121. At RT the BO3 groups occupy two inequivalent positions, B1 (D3) and B2 (C2). At 90 K the site symmetry of the B1 atoms is reduced to C2, whereas the site symmetry of the B2 atoms differentiates into a B2b (C2) and B2a (C1) (see also Table IVV). In the LT-phase, the angle between BO3 groups and the c-axis is changed. Moreover, in the LT-phase the BO3 groups in C1 position are considerably distorted and no longer flat (see Tab.IV). The LT structure is in agreement with the Raman data. The group theoretical vibrational analysis, based on the 90 K structure, shows that, due to the lowering of the symmetry, new librational modes of the BO3 become Raman active (R_x and R_y). The observed structural change is compatible with an appearance of the librational R_y mode of the BO3 group upon approaching T_s from above, and a subsequent hardening of this mode in the LT phase (See Fig3). Also the anisotropic displacement parameters (Table IIII) U_{33} of the oxygen atoms suggest that the borate groups are relatively free to oscillate around the c-axis.

Concerning the magnetic structure, the main peculiarity of both the RT and the 90 K structures is the existence of
FIG. 2: Coordination polyhedra for the RT ($R32$-(a)) and the LT ($P3_121$-(b)) structures of GdFe$_3$(BO$_3$)$_4$. At RT the Fe atoms with $C_2$-symmetry are coordinated by three different types of oxygen atoms. At 90 K there are two inequivalent positions for the Fe atoms: Fe1 (the same symmetry as RT) and Fe2, which is in a general position (surrounded by five different types of oxygen). At RT the Gd atoms are surrounded by six oxygens of one type ($D_3$-symmetry). At 90 K they are coordinated by three different types of oxygen atoms ($C_2$-symmetry). For the B atoms there are two kinds of coordination at RT. B1 (in $D_3$-symmetry) is surrounded by three oxygen atoms of the same type, the B1O$_3$-group is thus an equilateral triangle. The B2 atoms are surrounded by two types of O, B2O$_3$ is an isosceles triangle ($C_2$-symmetry). At 90 K there are three kinds of coordinations for the B atoms: B2bO$_3$ and B1O$_3$ are isosceles triangles ($C_2$ symmetry) and B2aO$_3$ is general triangle.

magnetically quasi-1D helicoidal iron chains (see Fig. 1). The intra-chain exchange interaction between the Fe ions is expected to be dominated by Fe-Fe direct exchange and Fe-O-Fe superexchange, depending respectively on Fe-Fe distance and two Fe-O-Fe angles (Fig. 4). Nevertheless there are some significant differences.

At RT all the Fe atoms are in equivalent positions ($C_2$). All Fe-chains are equivalent as are the Fe-O-Fe angles (102.40°(12) and 103.65°(8)) and Fe-Fe distances (3.1669(4) Å). Therefore, the exchange interactions between neighboring iron ions within a chain are also equivalent. At LT (Fig. 1), as shown in Table IV, the BO$_3$ groups form one general triangle (gray $C_1$ position) and two isosceles triangles (white and dark, $C_2$ position). At RT "gray" and "white" groups become also equivalent, with $C_2$ symmetry, and the "dark" one is a regular triangle with the $D_3$ symmetry. The reduction of the symmetry of the borate groups changes the surrounding of the Fe atoms (Fig. 2), yielding two inequivalent positions ($C_2$ and $C_1$). Therefore, the Fe-Fe distances are different for the two chains: one is stretched (3.1828(4) Å) and in the other one is compressed (3.1554(4) Å). The angles Fe-O-Fe for the first chain are 101.24°(5) and 103.71°(9), while those for the second are 102.46°(6) and 103.91°(8). Therefore also the intra-chain exchange interaction is different for the two chains.

The GdO$_6$ prism connects three chains, one containing Fe1-atoms with $C_2$ symmetry and two with Fe2-atoms in a general position. There is only one inequivalent position for the Gd-ions in both the RT and the 90 K structures. However, the site symmetry of the Gd-ions changes from $D_3$ at RT to $C_2$ at 90 K. This confirms the interpretation of the authors of Ref. 7, who interpreted low-temperature infrared spectra of Nd$_{0.01}$Gd$_{0.99}$Fe$_3$(BO$_3$)$_4$ in terms of Kramers doublets of Nd, assuming only one structural position for the Nd ions.

The detailed structure of the Fe-chains and their interconnection are shown in Fig. 1. The intra-chain interactions between Fe-atoms go through two Fe-O-Fe superexchange pathways. The magnetic inter-chain interaction arises from the Fe-O-O-Fe, and possibly the Fe-O-Gd-O-Fe superexchange path. The role of the first superexchange path is important because the substitution of Gd for non-magnetic Y does not lead to a disappearance of 3D magnetic
FIG. 3: Temperature dependence of Raman frequency of the low energy mode appearing at the structural phase transition $T_s$. Insert shows the low-frequency part of Raman spectrum at two close temperatures before and after phase transition.

FIG. 4: Two Fe-chains and the most important exchange paths: the intra-chain exchange is via Fe-Fe direct exchange or Fe-O-Fe super-exchange, while the inter-chain exchange is through Fe-O-Gd-Fe and Fe-O-O-Fe.

ordering. On the contrary, the Néel temperature for YFe$_3$(BO$_3$)$_4$, $T_{N1}=40$ K, is larger than the one found for Gd-compound ($T_{N1}=37$ K), and for NdFe$_3$(BO$_3$)$_4$ ($T_{N1}=30$ K)\cite{10}. Considering the different RE$^{3+}$ ionic radii (0.983 Å for Nd, 0.938 Å for Gd, and 0.900 Å for Y) it is clear that the Néel temperature of RFe$_3$(BO$_3$)$_4$ depends strongly on the ionic radii: a smaller ionic radius results in a higher $T_{N1}$. Moreover, $T_{N1}$ does not seem to be affected by the spin of the RE. In this sense it is clear that the main superexchange path of the interaction between different chains is the Fe-O-O-Fe path, and that a small distortion of this path changes substantially the magnetic properties of the system. It is therefore clear that the existence of two nonequivalent Fe chains with different Fe-Fe distances and Fe-O-Fe angles could lead to substantially different intra-chain exchange constant for the two chains\cite{20}, therefore it should be taken into account for the interpretation of the magnetic properties.

IV. CONCLUSIONS

In summary, we have determined the crystal structure of GdFe$_3$(BO$_3$)$_4$ at RT and 90 K. At RT GdFe$_3$(BO$_3$)$_4$ exhibits $R32$ structure, in agreement with Refs.\cite{1,3}. Below the structural phase transition ($T_s = 156$ K) the structure.
has the $P3_{1}21$ space group. The main difference of LT-structure compared to the RT one is the lowering of the symmetry and the tilt of the BO$_3$ groups. This confirms the interpretation of the Raman spectra of this phase transition. The main conclusion resulting from the LT structure determination is the presence of two inequivalent positions for the Fe atoms giving rise to two different iron helicoidal chains.

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