STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 75 (2019)

Supporting information for article:

Crystal structure and structural phase transition in bismuth-containing HoFe3(BO3)4 in the temperature range 11 – 500 K

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S1. Determining the occupancy of mixed Ho-Bi positions by step-by-step scanning

To determine the occupancy of the mixed Ho-Bi site, a step-by-step scanning of the Ho occupancy was performed for all complete data sets obtained using a CCD Xcalibur EOS S2 diffractometer at 90, 293, 350, 360, 365, 370, 380, 390 and 500 K. Step-by-step scanning was carried out using the ASTRA program designed for accurate single crystal diffraction analysis (A.P. Dudka, 2007). The least-square refinement carried out in ASTRA (Muradyan expert regime) showed the final holmium occupancy Q(Ho) = 0.93–0.96. The results of the step-by-step scanning of Q(Ho) are shown in Fig. S1. It was found that the curves at temperatures far from the phase transition (90, 293, 350 and 500 K) are fairly smooth and reliable. In the area of the structural phase transition, the curves become less reliable. The refinement of occupancy was sensitive to the correction for absorption and extinction. At 380 K, an attempt to plot a scanning curve failed. The temperature dependence of Q(Ho), obtained by step-by-step scanning, is shown in Fig. S3 (red line). The averaged occupancy of bismuth atoms [Q(Bi)=1-Q(Ho)] was 6(1)% for eight datasets.

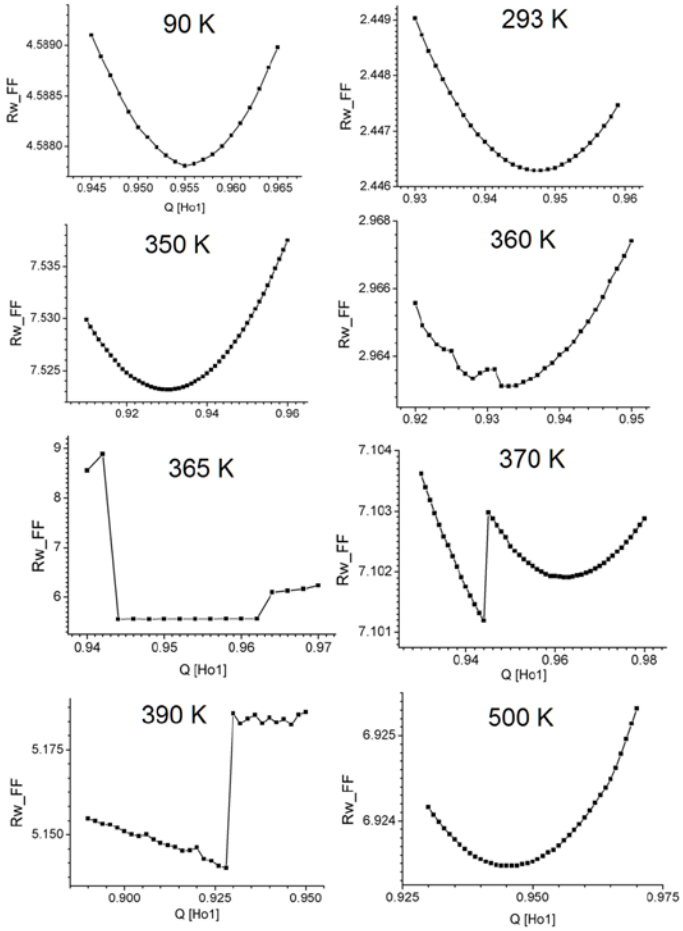

Figure S1 The dependence of reliability factor $R_w(F^2)$ on the occupancy of holmium atom at different temperatures.

S2. Determining the occupancy of mixed Ho-Bi site by a reduction of the contribution of anomalous scattering

Another way to determine the occupancy of mixed Ho-Bi site is to carry out the refinement of that with a reduction of the contribution of anomalous scattering along with the method of inter-experimental minimization (Dudka, 2008). This method is applicable to non-centrosymmetric crystals. It is well suited for refinement of $(Ho_{0.96}Bi_{0.04})Fe_3(BO_3)_4$, since this crystal belongs to non-centrosymmetric space groups both above and below the phase transition (*R*32 and $P3_121$ respectively) and we have enough data sets for experimental comparison.

The occupancy is refined in such a way that the difference in the intensities of the Friedel reflections, which are reduced by the contribution of anomalous scattering, becomes minimal. The Friedel law states that if the anomalous scattering effect is absent, X-rays are scattered with the same intensity in the forward and reverse directions (Okaya, 1970). In the absence of anomalous scattering (for example, when radiation of the appropriate wavelength is used), the calculated structural factors of the Friedel reflections will be the same for crystals of any symmetry. However, if a crystal consists of atoms of more than one chemical type and there is at least one anomalous scatterer, the effect of anomalous scattering causes violation of the Friedel law for non-centrosymmetric crystals. In the method described in this paper, an additional condition was used: the calculated structural factors of the Friedel reflections with the excluded contribution of anomalous scattering coincide. Consequently, the corresponding experimental structural factors also coincide.

The original data set averaged in sp. gr. $P3_121$ or sp. gr. *R*32 is divided into two reduced data sets with *hkl* and $\bar{h}\bar{k}\bar{l}$ reflections respectively, which can be considered independent. The intensities (the squares of the structure factors) of Friedel pairs for non-centrosymmetric crystals can be averaged after the anomalous scattering reduction. This roughly double reduced averaged data set can be used to refine the structural parameters.

Such a reduction can be carried out under the assumption that the reduced experimental structural factor F^0_{obs} refers to the initial experimental structural factor F^{an}_{obs}, since the calculated structure factor obtained without taking into account anomalous scattering F^0_{calc} refers to the general calculated structural factor F^{an}_{obs}:

$$F^0_{obs} = \frac{\left|F^{an}_{obs}\right|}{\left|F^{an}_{calc}\right|}\left|F^0_{calc}\right|. \qquad (1)$$

The superscript '*an*' refers to the included contribution of anomalous scattering, and the index '*0*' means that this contribution is excluded.

Another formula for reducing anomalous scattering takes into account the complex form of the structural factor (Takazawa at al., 1988):

- $$A_{obs\,(2L)} = \frac{\left|F_{obs}^{an}\right|}{\left|F_{calc}^{an}\right|} A_{calc}^{an} - (A_{calc}^{an} - A_{calc}^{0}), \qquad (2)$$
- $$B_{obs\,(2L)} = \frac{\left|F_{obs}^{an}\right|}{\left|F_{calc}^{an}\right|} B_{calc}^{an} - (B_{calc}^{an} - B_{calc}^{0}),$$

where $F=A+iB$ is the real and imaginary parts of the structural factor. It should be noted that the experimental structural factor in (2) is given in the kinematic scale, which means that the reduction value depends on the value of the scale factor and the correction for extinction.

Thus, for a known model of a crystal, the reduction of anomalous scattering is determined by the composition of the atoms entering the unit cell and the precision of fitting the model data to the experimental data. In the first approximation, these conditions can be met for crystals without impurities, all positions in which are completely filled if the refinement *R*-factors are within 0.5-2%. Such a reduction of anomalous scattering is often carried out in studies of charge density to construct electron density synthesis (Volkov *et al.*, 2006)). An expert of anomalous scattering reduction compares the intensities of Friedel reflections after elimination of anomalous scattering. The averaging factor *R* of the reduced Friedel intensities will be minimal for the correct occupancy.

Suppose that the occupancy of a holmium atom is Q [Ho] = *x*, then the scattering of a composite atom with allowance for anomalous scattering can be represented in a simplified form as

$$x\cdot F\,[\mathrm{Ho}] + x\cdot\Delta f'\,[\mathrm{Ho}] + i\cdot x\cdot\Delta f''\,[\mathrm{Ho}] + (1\text{-}x)\cdot F\,[\mathrm{Bi}] + (1\text{-}x)\cdot\Delta f'\,[\mathrm{Bi}] + i\cdot(1\text{-}x)\cdot\Delta f''\,[\mathrm{Bi}]$$

The described method was used for nine sets of diffraction data of $(Ho_xBi_{1-x})Fe_3(BO_3)_4$ crystal obtained at 90, 293, 350, 360, 365, 370, 380, 390 and 500 K. The adjusted occupation factor corresponds to the minimum value of the Friedel reflection averaging factor $R_{Friedel}$.

Figure S2 shows the averaging factor $R_{Friedel}$ dependence of the reduced squared modules of the Friedel reflection structure factor on the occupation factor for 9 sets of diffraction data. The final occupancy for the bismuth atom (fig. S3, blue line), equal to Q(Bi)=1-Q(Ho) for nine experiments, was 3.7±0.7 %. Some instability is still observed in the vicinity of the phase transition temperature.

The instability in determining the Bi-position occupancy is highest in the case of the conventional full-matrix refinement (fig. S3, black line). Step-by-step scanning reduces this instability. The anomalous scattering reduction expert makes the occupancy refinement the most stable, and the occupancy fairly consistent with values obtained using scanning regime of the X-ray energy-dispersive analysis.

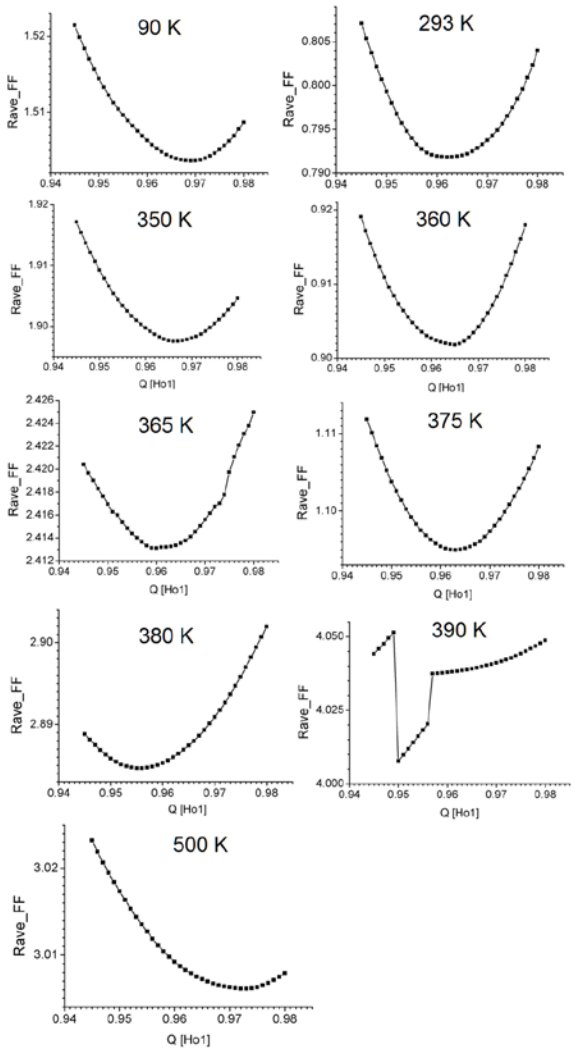

Figure S2 Dependence of reliability factor $R_{ave}(F^2)$ on the occupancy of holmium atom Q(Ho) in Ho-Bi 3a mixed site.

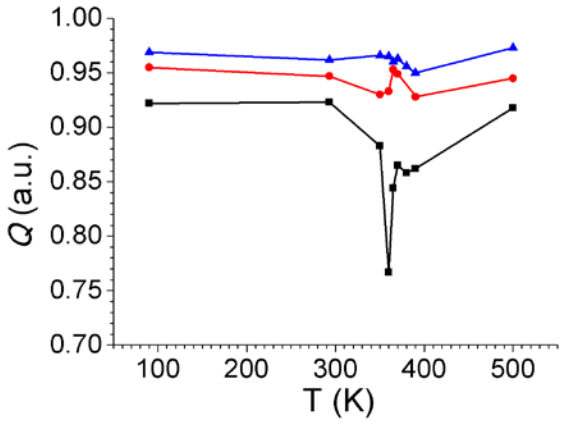

Figure S3 Temperature dependence of the Ho atom occupancy. The results of Jana2006 full-matrix least square refinement are shown by a black line. The red line indicates occupancy obtained by the step-by-step scanning. The blue line shows the results of refinement by the anomalous scattering reduction method.