Condensation of a tetrahedra rigid-body libration mode in HoBaCo$_4$O$_7$: the origin of phase transition at 355 K

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Abstract. Rietveld profiles, Mössbauer spectra and x-ray absorption fine structure (XAFS) were used to analyze the source of the structural phase transition at $T_s = 355$ K in HoBaCo$_4$O$_7$. Excess of oxygen content over ‘O$_7$’ was avoided by annealing the samples in an argon flow at 600 °C. Space groups (S.G.) $Pbn2_1$ and $P6_3mc$ were used to refine the structure parameters in the low- and high-temperature phases, respectively. Additionally, the $Cmc2_1$ symmetry was considered as a concurrent model of structure of the low-temperature phase. In the high-temperature phase, severe anisotropy of thermal motion of the majority of the oxygen atoms was observed. The variation of quadrupole splitting $\varepsilon$ near $T_s$ is not similar to the step-like anomaly frequently seen at the charge-ordering

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transition. We observe instead a dip-like anomaly of the average $\varepsilon$ near $T_s$. Narrow distribution of the electric field gradient (EFG) over different cobalt sites is observed. XAFS spectra show no evidence of significant difference between YBaCo$_4$O$_7$ ($T > T_s$) and HoBaCo$_4$O$_7$ ($T < T_s$). The origin of the transition at $T_s$ is ascribed to the condensation of the libration phonon mode associated with the rigid-body rotational movements of tetrahedra within the star-like tetrahedral units, the building blocks of the Kagomé network. It is shown that the condensation of the libration mode is not compatible with translation symmetry for the hexagonal S.G., but compatible for the orthorhombic S.G. The orthorhombic lattice parameters and EFG components ($V_{xx}$, $V_{yy}$ and $V_{zz}$) vary smoothly with temperature on approaching $T_s$. We argue that such a continuous variation supports the plausible scenario of librating tetrahedra, although the librational excitations propagate, most probably, differently than plane waves.
Figure 1. Perspective view of the quadruple unit cell in the low-temperature phase of REBaCo$_4$O$_7$. Kagomé and triangular layers of CoO$_4$ tetrahedra are marked by ‘K’ and ‘T’. The quadruple unit cell of HoBaCo$_4$O$_7$ is shown with atomic coordinates refined in the S.G. Pbn2$_1$.

REBaCo$_4$O$_7$ belongs to the family of swedenborgite, whose structure was solved by Pauling et al [5] in 1935. The swedenborgite SbNaBe$_4$O$_7$ was described as a net made up of star-like Be$_4$O$_{13}$ clusters [6], and similar Co$_4$O$_{13}$ stars can be found in REBaCo$_4$O$_7$. Two nonequivalent sites of Co exist in the high-temperature hexagonal phase [7, 8], but four Co sites exist in the low-temperature orthorhombic phase [8]. Clearly, some redistribution of charge should be associated with change of the symmetry. It remains under debate, however, whether or not the transition itself is driven by the charge redistribution.

Both phases consist of regular 1:1 stacking of Kagomé and triangular layers of CoO$_4$ tetrahedra (figure 1). In each of the phases, there are 75% of Co sites in Kagomé layers and 25% of Co sites in triangular layers. Each Co$_4$O$_{13}$ star thus involves three tetrahedra in K-layer and one in T-layer. We found relative arrangement of these stars to be unchanged; however, their exact geometry somewhat changes through $T_s$.

Analyzing the bond valence sums in both the low- and high-temperature phases, Huq et al [8] derived the preference of the Co site in the triangular layers for the Co$^{3+}$ ion at $T < T_s$, but, contrarily, for the Co$^{2+}$ ion at $T > T_s$. On the other hand, it was argued recently [9] that the Co sites in triangular layers are generally exhibiting shorter Co–O distances than the sites in Kagomé layers, irrespective of the transition at $T_s$; the Co$^{3+}$ ions should always prefer the site in triangular layers.

In this work, we investigate the phase transition in HoBaCo$_4$O$_7$ using synchrotron diffractometry, Mössbauer spectroscopy and x-ray absorption fine structure (XAFS). It was verified that substitution of 2.5% of Co with Fe did not introduce a significant change of $T_s \approx 355$ K. We observed only very small changes in Mössbauer spectra through $T_s$ and we argue that no charge ordering takes place at the phase transition. Different symmetry groups
were tested to fit the phases below $T_s$ ($Cmc_2$ and $Pbn2_1$) and above $T_s$ ($P6_3mc$ and $P31c$). From the results of our structural study, the origin of the phase transition is understood to be unrelated to charge redistribution. We consider instead the double-well potential models [10], in which the transition can be explained as the condensation of a libration phonon mode associated with the rigid-body motion of the tetrahedra in Kagomé layers around the center of the above-mentioned $Co_4O_{13}$ stars. Following this scenario of the displacive phase transition, we explain the dip-like temperature dependence of the Mössbauer spectra quadrupole splitting around $T_s$ according to the correlations between the electric field gradient (EFG) components known to occur through the continuous phase transitions [11].

2. Experimental

The samples of $HoBaCo_4O_7$ and $HoBaCo_{3.9}Fe_{0.1}O_7$ were prepared from $Ho_2O_3$, $BaCO_3$, $Co_3O_4$ and $^{57}Fe_2O_3$ powders using standard ceramic synthesis technology at 1100 °C. One sample of $YBaCo_4O_7$ for the XAFS study was also prepared using $Y_2O_3$ in the same conditions. The sample of $HoBaCo_4O_7$ was made first in Japan and exactly the same synthesis was reproduced in Russia. Two samples showed the reproducible values of $T_s$ and lattice parameters. Other samples, doped with $^{57}Fe$, were prepared in Russia. Final annealing in a flow of pure Ar gas was always done at 600 °C.

Measurements of x-ray diffraction patterns for Rietveld analysis were conducted at the ‘Anomalous Scattering’ beamline of the VEPP-3 storage ring in the Siberian Synchrotron Radiation Centre (SSRC). The beamline is equipped with an Si (111) monochromator on the primary beam and a Ge (111) crystal analyzer on the diffracted beam. Three patterns of $HoBaCo_4O_7$ were measured at 300 K for three wavelengths shown in figure 2(a). The fourth pattern was measured at 380 K for λ = 1.5421 Å. The structure parameters were refined through the analysis of full-profile x-ray diffraction intensities using FULLPROF program [12, 13]. Anomalous dispersion corrections for the atomic scattering factors of Ho, Ba and Co were introduced into the input files of FULLPROF using the Brenann and Cowan data from DispAnoV2 program.

Measurements of x-ray diffraction patterns in the temperature range between 27 and 113 °C were also conducted, using an MXP21 Mac Science diffractometer with the following operation conditions: $50^\circ < 2\theta < 60^\circ$ with the step size of 0.02°, Cu-K$_\alpha$ radiation ($\lambda = 1.5405$ and 1.5443 Å), $V = 45$ kV and $I = 100$ mA. The lattice parameters were refined using a Rietveld analysis.

The Co K-edge XANES spectra were measured at the EXAFS station of SSRC. The beam was monochromatized with a channel-cut Si (111) monochromator. The energy resolution was 0.8 eV.

Mössbauer spectra were collected with the velocity-reversive spectrometer NZ-640 (Hungary), using the regime of constant acceleration for a moving source of $^{57}Co$ embedded in a metal (Cr) matrix. The chemical shifts are given relative to Fe metal. The temperature of the sample was maintained with an accuracy of $\pm 0.1^\circ$. The Mössbauer source was kept at room temperature ($24 \pm 1$ °C). In this setup, the drift of the source temperature had to be taken into account only in the temperature dependencies of the chemical shift. Mössbauer spectra were measured in the range of velocities from $-4$ to $4$ mm s$^{-1}$ and stored into 1000 channels equidistributed in velocity. In each of the 27 spectra obtained, the number of counts per channel was approximately $10^6$. 

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Figure 2. Three wavelengths used in the diffraction experiments shown on the plot of theoretical atomic scattering factor corrections $f'$ and $f''$ for Co and Ho (a); characteristic area of the high-resolution synchrotron x-ray diffraction patterns (Rietveld plots) at $\lambda = 1.5421$ Å in the high-temperature (b) and low-temperature (c) phases of HoBaCo$_4$O$_7$. The structure of the low-temperature phase was refined at $T = 300$ K using either S.G. $\text{Pbn}2_1$ or $\text{Cmc}2_1$, one of which ($\text{Pbn}2_1$) is shown in (c). Theoretical positions of the permitted reflections are shown in (c) for both $\text{Pbn}2_1$ and $\text{Cmc}2_1$ groups. Indicated by the arrow, reflection (105) is among the very weak peaks extinguished for S.G. $\text{Cmc}2_1$, but allowed for S.G. $\text{Pbn}2_1$.

3. Results

Differential thermal analysis results have revealed the highest temperature of structural transition $T_s = 355$ K for HoBaCo$_4$O$_7$ among all the previously studied cobaltites of the
Figure 3. The curves of differential thermal analysis in HoBaCo$_4$O$_7$ measured upon heating and cooling at a rate of $3\, {\text{°C}}\, \text{min}^{-1}$.

The RBaCo$_4$O$_7$ series (R = Lu, Yb, Tb, Er or Y) (cf [1]–[3]). The DTA curve collected at the cooling/heating rate of 3 K min$^{-1}$ showed the endothermic effect at the temperature $T_s$ of 82 °C for sample heating (figure 3). The latency interval, within which the high-temperature phase can be undercooled, evidences the first-order character of the transition in agreement with the general renormalization group theory of the phase transitions (see, for example, the references in the review [10]).

The spacing between heating and cooling curves is collapsed in figure 4, where the temperature dependence of the lattice parameters is shown. All the data of figure 4 were obtained using the overnight program, so that the average rate of the temperature ‘sweep’ was slower by two orders of magnitude than that in figure 3.

3.1. Structure refinements

The lattice parameters below and above $T_s$ were refined using Rietveld analysis. To refine the lattice parameters and atomic coordinates at $T < T_s$, we used previously suggested structure models based on the S.G. $Cmc2_1$ [1] and $Pbn2_1$ [8]. The substitution of 2.5% Co with Fe has no significant effect on the lattice parameters. In HoBaCo$_4$O$_7$ we obtained $a = 6.3013(1)$ Å, $b = 10.9552(2)$ Å and $c = 10.2225(2)$ Å. In the Fe-doped sample HoBaCo$_{3.9}$Fe$_{0.1}$O$_7$, we obtained at room temperature the orthorhombic cell with $a = 6.3006(3)$ Å, $b = 10.9573(5)$ Å and $c = 10.2275(5)$ Å.

The temperature evolution of the lattice parameter $a$ and the reduced lattice parameter $b/\sqrt{3}$ shows that there exists below $T_s$ a wide temperature range ($\Delta T = 30–40$ K), in which the orthorhombic distortion gradually increases at cooling. This behavior contrasts with the
Figure 4. Evolution of the lattice cell parameters $a$, $b/\sqrt{3}$ and $c$ with temperature near the structural phase transition.

abrupt jumping of the $a$ parameter, reported for YbBaCo$_4$O$_7$ [4]. The $c$ parameter, in contrast, exhibits a smaller jump at $T_s$ in our figure 4, as compared to its jump reported previously for YbBaCo$_4$O$_7$ [4].
Three patterns measured on synchrotron radiation at 300 K were fitted altogether, varying at once the different profile parameters particular for each pattern and the atomic coordinates common for all patterns. The results shown in table 1 were obtained with the S.G.’s Pbn21 and Cmc21. Corresponding reliability factors are $\chi^2 = 3.83$, $R_{1,Bragg}^{\text{obs}} = 7.4\%$, $R_{1,iso}^{\text{obs}} = 7.7\%$, $R_{0,6999}^{\text{obs}} = 9.3\%$ for Pbn21, and $\chi^2 = 3.91$, $R_{1,Bragg}^{\text{obs}} = 7.1\%$, $R_{1,iso}^{\text{obs}} = 7.2\%$, $R_{0,6999}^{\text{obs}} = 9.9\%$ for Cmc21. Pattern weight factors proportional to the total number of counts per pattern were used. Quite similar results were found on varying the weight factor in the broad area of the triangular two-dimensional (2D) space of the weight factors.

The use of multiple wavelengths allowed us to vary the contribution of certain atoms to the diffraction patterns. Diffraction intensities around the angles of strongest peaks (2$\Theta$ $\sim$ 30–40$^\circ$) are modified by anomalous scattering in such a way as if either Ho or Co was isomorphously replaced with La or Ti, respectively; in effect, as if the hypothetical compounds LaBaCo$_3$O$_7$ and HoBaTi$_3$O$_7$ were measured additionally to HoBaCo$_3$O$_7$. Figure 5 shows the Rietveld plot of HoBaCo$_3$O$_7$ at the wavelength near the Co K-edge. The inset shows the difference between two resonant patterns measured near the Co and Ho absorption edges. These differential patterns consist of observed and theoretical profiles $\Delta I_{\text{obs}}$ and $\Delta I_{\text{theor}}$ at the profile conditions of the resonant pattern at the Co K-edge. To plot the inset patterns the profiles $I_{\text{obs}}$ and $I_{\text{theor}}$ for $\lambda = 1.5421$ Å were first transformed to the profile conditions of the profiles $I_{\text{obs}}$ and $I_{\text{theor}}$ for $\lambda = 1.6134$ Å and then subtracted from the latter. The difference between experimental and theoretical differential patterns is largest in the vicinity of the strongest peak given by the overlapped (023) and (113) reflections. In terms of both the Pbn21 and Cmc21

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textit{Pbn21} & \textit{Cmc21} & $x$ & $x$ & $y$ & $y$ & $z$ & $B_{\text{iso}}$ & $B_{\text{iso}}^2$ \\
\hline
Ho & 0.0014(5) & 0 & 0 & 0.6672(2) & 0.6664(2) & 0.8717(2) & 0.8720(1) & 1.4(2) & 1.3(2) \\
Ba & 0 & 0 & 2/3 & 2/3 & 1 & 1/2 & 1/2 & 1.4(2) & 1.4(2) \\
Co & $-0.011(1)$ & 0 & 0 & $-0.0055(6)$ & 0.0067(4) & 0.9409(4) & 0.9388(4) & 0.7(2) & 0.9(2) \\
Co & $-0.001(1)$ & 0 & 0 & 0.1747(2) & 0.1770(2) & 0.6996(4) & 0.6985(4) & 0.6(4) & 0.5(2) \\
Co & 0.257(1) & – & 0.0879(4) & – & 0.1891(6) & – & 1.1(4) & – \\
Co & 0.252(1) & 0.2525(4) & 0.9239(4) & 0.9177(2) & 0.6819(6) & 0.6871(4) & 1.0(4) & 1.1(3) \\
O1 & 0.008(4) & 0 & 0 & $-0.003(2)$ & 0.0122(9) & 0.2555(7) & 0.2535(7) & 1.7(7) & 1.0(5) \\
O2 & 0.783(2) & – & 0.2648(14) & – & 0.7793(10) & – & 0.9(7) & – \\
O2 & $-0.003(5)$ & 0 & 0.4860(9) & 0.4784(7) & 0.2400(13) & 0.2238(7) & 0.6(7) & 0.4 \\
O2 & 0.735(2) & 0.763(1) & 0.7512(14) & 0.7395(7) & 0.2273(12) & 0.2600(6) & 0.5(7) & 1.6 \\
O1 & $-0.053(2)$ & 0 & 0.1535(11) & 0.1439(6) & 0.5116(16) & 0.5077(9) & 0.4(6) & c \\
O2 & 0.224(2) & – & 0.0983(12) & – & 0.0141(22) & – & 1.5(9) & – \\
O3 & 0.254(3) & 0.250(1) & 0.9355(11) & 0.9193(9) & 0.5064(22) & 0.5166(8) & 1.5(9) & d \\
\hline
\end{tabular}
\caption{Atomic coordinates for HoBaCo$_3$O$_7$ at 300 K.}
\end{table}

\\textsuperscript{a}Anisotropic thermal displacement factors (ATDF) were refined for O31 and O33 in S.G. Cmc21.
\textsuperscript{b}Position multiplicity 8 in the S.G. Cmc21. All other positions in both Pbn21 and Cmc21 groups have the multiplicity 4.
\textsuperscript{c}Refined ATDF for O31: $U_{11} = 0.13(2)$, $U_{22} = 0.016(8)$, $U_{33} = 0.004(9)$, $U_{12} = -0.006(8) \text{Å}^2$. The values of $U_{13}$ and $U_{23}$ are fixed at 0 by symmetry. $U_{ij}$ are smaller than $B_{ij}$ by a factor of 8$\pi^2$.
\textsuperscript{d}Refined ATDF for O33: $U_{11} = 0.033(17)$, $U_{22} = 0.09(3)$, $U_{33} = 0.028(17)$, $U_{12} = 0.01(2)$, $U_{13} = -0.01(2)$ and $U_{23} = -0.05(3) \text{Å}^2$. 

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The conventional (main panel) and differential (inset) Rietveld plots for the synchrotron x-ray diffraction data collected at $T = 300$ K (below the phase transition) in HoBaCo$_4$O$_7$. The main panel: observed, calculated and difference intensities near the Co K-edge ($\lambda = 1.6134$ Å). Inset: the differences $I_{\text{obs}}(\text{CoK}) - I_{\text{obs}}(\text{HoL_{III}})$ and $I_{\text{theor}}(\text{CoK}) - I_{\text{theor}}(\text{HoL_{III}})$, where the profile $I_{\text{theor}}(\text{HoL_{III}})$ was transformed to the $I_{\text{theor}}(\text{CoK})$ profile conditions.

Among the orthorhombic swedenborgites, several compounds were refined previously with the S.G.’s $Pbn2_1$ and $Cmc2_1$. The S.G. $Cmc2_1$ was found first to suit the structure of a Zn-based swedenborgite [14]. Later, the x-ray diffraction patterns of REBaCo$_4$O$_7$ for a number of RE were indexed with the orthorhombic cell of the $Cmc2_1$ symmetry [1]. We observed a few unindexed extra diffraction peaks, such as the reflection (105) in figure 2, which could be indexed within the S.G. $Pbn2_1$ suggested recently for YbBaCo$_4$O$_7$ [8]. Since the intensity of the extra reflections is extremely small, their occurrence has, in fact, a very small effect on the result of refinement. Therefore the $R$-factors are quite similar and even better sometimes for $Cmc2_1$ than for $Pbn2_1$. The results for both $Pbn2_1$ and $Cmc2_1$ symmetries are shown in table 1. The resulting structure in terms of $Pbn2_1$ is similar to that of YbBaCo$_4$O$_6.95$ at 150 K [8]. The structure refined in terms of $Cmc2_1$ is shown in figure 6.

In the higher-symmetry phase above $T_s$, there are three nonequivalent oxygen sites. We call O1 the oxygens in the center of the star Co$_4$O$_{13}$. Other oxygens at the bottom of K-layer in figure 1 are called O2 and those on top of K-layer are called O3. The atoms of cobalt and oxygen in tables 1–3 are denoted, depending on the S.G., by single or double indices to simplify the
Figure 6. Triple unit cell of HoBaCo$_4$O$_7$ refined with the symmetry group $Cmc2_1$ and viewed along [001]. The anisotropic thermal displacement factors refined for the atoms O31 and O33 are represented by the surface of 50% probability.

Comparison between the low- and high-temperature phases. In the high-temperature phase, there occur just two inequivalent positions for Co, labeled as Co1 and Co2. On lowering symmetry in the low-temperature phase, each of Co2, O2 and O3 splits into two ($Cmc2_1$) or three ($Pbn2_1$) positions. Then the second index is added for these positions.

Interatomic distances for the first coordination spheres in the low-temperature phase are shown in Table 2. Obtained for the S.G. $Pbn2_1$($Cmc2_1$) average distances Co1–O and Co2–O are 1.892 (1.900) Å and 1.918 (1.900) Å, respectively. Average Co–O distances for different Co sites in the Kagomé layer are $\langle d \rangle_{Co21-O} = 1.921$ (1.958) Å, $\langle d \rangle_{Co22-O} = 1.907$ Å and $\langle d \rangle_{Co23-O} = 1.926$ (1.871) Å. Some preference of the Co1 site for Co$^{3+}$ ions can be suggested only for the S.G. $Pbn2_1$; however, any charge stratification between K- and T-layers cannot induce orthorhombicity. Therefore, the hypothesis of charge ordering is implausible within the $Pbn2_1$ model. In the $Cmc2_1$ model, the state with Co$^{3+}$ placed in the smallest Co23 site is not a degenerated state because of the double multiplicity of this site compared to the multiplicities of the remaining Co1 and Co21 sites. Therefore, neither $Pbn2_1$ nor $Cmc2_1$ models fit the idea of charge ordering.

We suggest another origin of the orthorhombicity, which is related to locking the rotational motion of tetrahedra in Kagomé layers. This motion is visualized with the use of anisotropic thermal factors in figures 6 and 7. Within the refinement of isotropic thermal factors, the obtained $B_{iso}$ were too unrealistic (>4 Å$^2$) for several oxygen atoms in the structural models based on the S.G.’s $Cmc2_1$ ($T < T_c$) and $P6_3mc$ ($T > T_c$). Therefore, in these models, the anisotropic motion was allowed at fitting the thermal displacement factors of the O2 and O3 atoms. This was not necessary for the $Pbn2_1$ model ($T < T_c$). One thus observes at cooling...
Table 2. Cation-oxygen bond lengths for all Ho, Ba and Co cations in HoBaCo$_4$O$_7$ at 300 K.

| Bond   | $Pbn_2_1$ | $Cmc_2_1$ | Bond   | $Pbn_2_1$ | $Cmc_2_1$ | Bond   | $Pbn_2_1$ | $Cmc_2_1$ |
|--------|-----------|-----------|--------|-----------|-----------|--------|-----------|-----------|
| Ho–O21 | 2.291(13) |           | Ba–O23 |           |           | Co21–O1| 1.973(15) | 2.144(8)  |
| Ho–O22 | 2.152(12) | 2.190(8)  | Ba–O31 |           | 2.819(10) | 3.162(5)| Co21–O21 | 1.867(15) |
| Ho–O23 | 2.269(14) | 2.264(7)  | Ba–O31 |           | 3.494(10) | Co21–O23| 1.882(16) | 1.853(7)  |
| Ho–O31 | 2.452(14) | 2.499(7)  | Ba–O32 |           | 2.940(14) | Co21–O31| 1.963(17) | 1.98(1)   |
| Ho–O32 | 2.383(18) |           | Ba–O32 |           | 3.387(14) | Co22–O1| 1.979(15) |           |
| Ho–O33 | 2.363(18) | 2.357(9)  | Ba–O33 |           | 2.970(13) | 3.141(1)| Co22–O21| 1.866(15) |
|        |           |           |        |           |           |        |           |           |
| Ba–O21 | 2.742(11) |           |        |           |           |        |           |           |
| Ba–O22 | 2.534(12) |           |        |           |           |        |           |           |
| Ba–O22 | 2.969(12) | 2.785(8)  | Co1–O1 | 1.897(8)  | 1.910(9)  | Co23–O1| 1.996(15) | 1.892(5)  |
| Ba–O22 | 3.313(13) | 3.498(8)  | Co1–O32| 2.011(17) |          | Co23–O22| 1.977(15) | 1.883(8)  |
| Ba–O23 | 2.900(13) | 2.979(6)  | Co1–O33| 1.840(17) | 1.945(1)  | Co23–O33| 1.802(23) | 1.739(9)  |

The indicated bond lengths have double abundance in the S.G. $Cmc_2_1$ due to the multiplicity 8 for the positions of Co23, O23 and O33.

Table 3. Atomic coordinates for HoBaCo$_4$O$_7$ at 380 K obtained within the S.G. $P6_3mc$.

| Atom | $x$  | $y$  | $z$  | $B_{iso}^a$ |
|------|------|------|------|-------------|
| Ho   | 2/3  | 1/3  | 0    | 0.4(3)      |
| Ba   | 2/3  | 1/3  | 0.6258(7) | 1.5(3)      |
| Co1  | 0    | 0    | 0.569(3)  | 0.4(2)      |
| Co2  | 0.1705(7) | −0.1705(7) | 0.805(2) | 0.4(2)      |
| O1   | 0    | 0    | 0.357(5)  | 1.8(9)      |
| O2   | 0.498(3) | −0.498(3) | 0.852(4) | b           |
| O3   | 0.837(3) | −0.837(3) | 0.131(4) | c           |

Anisotropic thermal displacement factors were refined for O1 and O3.

$U_{11} = U_{22} = 0.026(9), U_{33} = 0.07(1), U_{12} = 0.02(1), U_{13} = −U_{23} = −0.005(5)$ Å$^2$.

$U_{11} = U_{22} = 0.12(2), U_{33} = 0.01(1), U_{12} = 0.11(2), U_{13} = −U_{23} = −0.002(4)$ Å$^2$.

through $T_c$ locking the rotational motions in the O3 sites only for the $Cmc2_1$ model, but in both O2 and O3 sites for the $Pbn2_1$ model. In the high-temperature phase $P6_3mc$, the correlated motion in the O2 and O3 sites can be thought of as a rigid-body libration of the CoO$_4$ tetrahedron. Such a rigid-body picture cannot be contemplated for the $Cmc2_1$ model, in which only the O31 and O32 sites showed unusual thermal displacement factors. Related large deformations of tetrahedra are unlikely. Therefore, in the rest of this paper, the $Pbn2_1$ model of the low-temperature phase will be considered in more detail.

The lattice parameters refined at $T = 380$ K are $a = 6.3046(2)$ Å and $c = 10.2604(4)$ Å. The S.G.’s $P31c$ and $P6_3mc$ were examined and gave quite similar parameters of fitting quality. In table 3, the atomic coordinates obtained within the S.G. $P6_3mc$ are shown. In a recent study
Figure 7. [001] projections of the crystal structure in high (top panel) and low (middle panel) phases in HoBaCo₄O₇ obtained in this work and in YbBaCo₄O₇ (bottom panel, constructed for comparison according to the data of [8]).

of single crystals of HoBaCo₄O₇ [15], the arguments in favor of the latter S.G. were obtained by observing the equal intensities of symmetry-equivalent reflections. For example, the reflections (101) and (011) are symmetry-equivalent. Such distinguishables in single crystal reflections should have different intensities for $P31c$. In our Rietveld refinements with both the S.G.’s $P6₃mc$ and $P31c$, we found while using $B_{iso}$ that the S.G. $P31c$ permits us to reach a better fit than the S.G. $P6₃mc$. However, with the S.G. $P6₃mc$, the equally good fitting quality parameter ($R_{Bragg} = 5.65$) was readily obtained through introducing the anisotropic factors of thermal
displacements $B_{ij}$ for O1 and O3 atoms. The refined anisotropic parameters for these atoms are shown as footnotes under table 3 and depicted in the top panel of figure 7.

In the high-temperature phase, we found the average distances Co1–O and Co2–O of 1.96(2) Å and 1.86(2) Å, respectively. From low- to high-temperature phases, we observe, irrespective of the S.G. assumed for the low-temperature structure, that the average Co2–O distances are shortened, while the average Co1–O distances are elongated. Especially, for the S.G. Pbn21, each of the Co sites in the Kagomé layer is larger for $T < T_s$, but the opposite is true for $T > T_s$. The larger size for the Co1 site, $\langle d\rangle_{\text{Co1–O}} > \langle d\rangle_{\text{Co2–O}}$ is the argument against the larger valence of Co1 than that of Co2. The same trends were noticed by Huq et al [8], although these authors have refined the high-temperature structure with the S.G. P31c. We note, however, that the cobaltites REBaCo$_x$O$_7$, in which a larger valence was found for Co1 than for Co2 [9], did not show any structural phase transition. Judging from the relationship between $\langle d\rangle_{\text{Co1–O}}$ and $\langle d\rangle_{\text{Co2–O}}$, such transitionless cobaltites must be ‘in the low-temperature phase’ vanishing by some means of structural distortion. The observed inversion of this relationship at heating through $T_s$ has inspired our effort to search for the changes across $T_s$ in the spectra of XAFS and Mössbauer.

3.2. X-ray absorption spectra near Co K-edge

The XAFS spectra of HoBaCo$_x$O$_7$ and YBaCo$_{4-x}$Fe$_x$O$_7$ ($x = 0$ and 0.1) are very similar (figure 8). The XANES begins with a pre-edge peak at $E = 7710$ eV followed by the main edge and the ‘white line’ maximum of absorption at 7730 eV. These pre-edge peak and white lines correspond to the electron transitions from 1s orbital to the 3d and 4p bands, respectively. Derivative spectroscopy using the second derivative of XAFS ensures the effective enhancement of resolution, which can be useful to separate two or more overlapping subbands. The pre-edge peak in the tetrahedrally coordinated Co site is composed of the vacant orbitals situated in the $e_g$ and $t_{2g}$ subbands. Even if they are unresolved in the pre-edge peak as wide as 5 eV, taking the second derivative of the XAFS spectra could be useful to resolve them as the separated minima of $\partial^2\mu/\partial E^2$. In an octahedral Co site of La$_{1-x}$Sr$_x$CoO$_3$, for example, such a manipulation allows us to resolve the $e_g$ and $t_{2g}$ subbands separated by 2.5 eV [16].

Because our XAFS station was not equipped with a furnace, all measurements were done at 300 K. Instead of measuring the spectra of an REBaCo$_x$O$_7$ across the phase transition, the spectra were measured for RE = Ho and Y with $T_s = 355$ K and 280 K, respectively. The only difference between the spectra for RE = Ho and Y is that the high-energy shoulder of $\partial^2\mu/\partial E^2$ near $E = 7712$ eV is better articulated in the low-temperature phase (RE = Ho). In a tetrahedral coordination, the $e_g$ subband lies lower in energy than the $t_{2g}$ subband. Therefore, for the high-spin Co$^{2+}$($d^5$) the $e_g$ orbitals are full and the $t_{2g}$ orbitals are half-filled. The predominant minimum of $\partial^2\mu/\partial E^2$ should be ascribed to the $t_{2g}$ orbitals of the high-spin Co$^{2+}$ associated with 75% of the total pre-edge peak area. The remaining 25% are due to Co$^{3+}$. The K-edge Co$^{3+}$ is expected to move to higher energy as a whole, including the pre-edge peak, by about 2 eV. In the high-spin (HS) state of the tetrahedrally coordinated Co$^{3+}$, the splitting of the pre-edge peak is expected, since one half-filled orbital appears in the $e_g$ subzone; however, in the intermediate-spin (IS) state of such Co$^{3+}$, the pre-edge peak is unsplit again as it would come entirely from the transition 1s $\rightarrow$ 3d($t_{2g}$). Therefore, the feature near $E = 7712$ eV must be better pronounced.

8 The $T_s$ value for our YBaCo$_{4-x}$O$_7$ was lower by 20 K than $T_s$ in YBaCo$_x$O$_7$ synthesized by Caignaert et al [3] probably, owing to slightly different conditions of final annealing.

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Figure 8. XANES spectra at the Co K-edge and the second XANES derivatives in the region of the pre-edge peak for HoBaCo$_4$O$_7$ (1), YBaCo$_4$O$_7$ (2) and YBaCo$_{3.9}$Fe$_{0.1}$O$_7$ (3).

for the lower spin state of Co$^{3+}$. Comparing the Seebeck coefficient measured in YbBaCo$_4$O$_7$ with theoretically predicted spin-dependent values, Maignan et al [4] found that both Co$^{2+}$ and Co$^{3+}$ are in HS states. Our spectra are consistent with the HS states of Co$^{2+}$ and Co$^{3+}$, although the presence of some IS Co$^{3+}$, especially in the low-temperature phase, cannot be excluded.

3.3. Mössbauer spectroscopy

Our Mössbauer spectra collected in the temperature range between ambient temperature and 133 °C consist of two series. Firstly from one measurement to another, the temperature was ascending. In the second series, the measurements were made for a sequence of temperatures at cooling the sample. All the obtained spectra are quite symmetric doublets (figure 9). Spectra treatments are in an order that would take into account the occurrence of four nonequivalent sites for the Fe dopants at $T < T_s$ and two sites at $T > T_s$. However, to date, it has been feasible only to fit each spectrum with either a two-doublet or one-doublet (averaged) envelope. In the two-doublet spectra treatment, the following parameters of the doublets were obtained at room temperature: $\delta_1 = 0.182$ mm s$^{-1}$; $\epsilon_1 = 0.389$ mm s$^{-1}$ and $\Gamma_1 = 0.342$ mm s$^{-1}$ for the majority (80%) subspectrum, and $\delta_2 = 0.193$ mm s$^{-1}$; $\epsilon_2 = 0.693$ mm s$^{-1}$ and $\Gamma_2 = 0.351$ mm s$^{-1}$ for the minority (20%) subspectrum.

In the studied range of temperatures 297 K $\leq T \leq$ 406 K, the average quadrupole splitting is varied by only $\simeq 0.01$ mm s$^{-1}$. In such a narrow range, the determination of the behavior of the spectral parameters was feasible first of all due to the high accuracy of our experimental setup. Secondly, a special analysis of the Mössbauer data treatments was performed. Namely, the accuracy of determination of spectral parameters in each spectrum was taken into account as described below.
3.3.1. Defining the generalized spectral parameters and their accuracy. Parameters of the Mössbauer spectra were determined by a standard technique via minimizing the value of $\chi^2$:

$$\chi^2 = \sum_{i=1}^{N} \frac{[F_{\text{ex}}(i) - F_{\text{th}}(i; a)]^2}{\sigma_i^2}, \quad \sigma_i = \sqrt{F_{\text{ex}}(i)},$$  

i.e. finding the vector of parameters $a$ of the theoretical spectrum $F_{\text{th}}(i; a)$, such that $\chi^2 = \text{min}$. In this work, for all spectra, we adopted the generalized treatment, in which the parameter vector $a$ was represented by only four elements: (i) average number of counts at infinite velocity, (ii) chemical shift $\delta$, (iii) quadrupole splitting $\varepsilon$ and (iv) linewidth of the lines of the doublet. Here $i = 1, \ldots, N$ are the experimental points, $F_{\text{ex}}(i)$ is the number of counts in the $i$th channel and $\sigma_i$ is the evaluation of the dispersion in the experimental spectrum.

During the spectra measurements in this work, the spectrometer operating time up to 1 month has been reached; however, the errors in determining the parameters from the minimization of $\chi^2$ in each spectrum (equation (1)) do not involve any drifts and/or uncontrolled instabilities related to a long-term experimental run. In order to estimate the relative contributions of the long-term sources of the errors, the following procedure was adopted. Firstly, we assumed that the chemical shift must depend on the temperature linearly as does the so-called second-order-Doppler (SOD) shift, or 'red shift'. Therefore, we fitted 27 obtained values of the chemical shift with the straight line. The errors of chemical shift $\Delta_n^2$ obtained from nonlinear regression of each of these 27 spectra (equation (1)) were used in this linear fit. As a result, we obtained an estimate of the squared deviation of the experimental chemical shift values (i.e. $\delta(n)$ as a component of the parameter vector $a$ in equation (1)) from the linear temperature dependence hypothesis:

$$\chi^2(\{\Delta_n^2\}) = \sum_{n=1}^{S} \frac{[\delta(n) - A - BT_n]^2}{\Delta_n^2}. \quad (2)$$
Here $S = 27$, $A = 0.198 \text{ mm s}^{-1}$ and $B = -6.38 \times 10^{-4} (\text{ mm s}^{-1}) \text{ K}^{-1}$ are the parameters of the linear temperature dependence of the chemical shift, obtained by minimizing the value of $\chi^2$ in equation (2). The value of $A$ refers to $T = 273 \text{ K}$.

It was supposed then that the uncontrolled long-run instabilities of the spectrometer can be taken into account by introducing a coefficient $\eta$ according to the following substitution: $\Delta_n^2 \to \eta^2 \Delta_n^2$. The value of $\eta$ can be estimated in the condition that the minimum of $\chi^2$ from equation (2) reaches its theoretical value when $\Delta_n^2$ is replaced with $\eta^2 \Delta_n^2$:

$$\chi^2(\{\eta^2 \Delta_n^2\}) = S - 2. \quad (3)$$

Here $S - 2$ is the number of degrees of freedom for the random variables in equation (2). The calculation performed according to this procedure has led to the result $\eta = 1.6$. Next, the errors in estimation of the chemical shifts and quadrupole splitting parameters were multiplied by the coefficient $\eta$. The result of this operation is shown in figure 10. Finally, our analysis resulted in the average error of the quadrupole splitting not exceeding 0.0017 mm s$^{-1}$. The presented analysis thus suggests that the observed variation of $\varepsilon$ near $T_s$, although small, is the intrinsic and reproducible property of the material.

3.3.2. Narrowness of the EFG distribution over different cobalt sites. The observed quadrupole splitting varies within 3% in the range $\pm \Delta T/T_s = 20\%$. The generalized procedure for analyzing the Mössbauer spectra allowed us to treat in the same way the spectra above and below $T_s = 355 \text{ K}$. Despite the very good statistical quality of our spectra, introducing the second doublet produces no significant improvement of fitting quality. More detailed treatments of our spectra, to be presented elsewhere, would take into account the occurrence of four nonequivalent sites for Co at $T < T_s$ and two sites for Co at $T > T_s$. Recently, two subspectra were resolved at 4 K in YBaCo$_{3.96}$Fe$_{0.04}$O$_{7.02}$ owing to a difference of magnetic hyperfine fields $\Delta B_{hf} = 3 \text{ T}$ [17]. The authors claimed that the Mössbauer spectra cannot resolve the difference between the sites Co21, Co22 and Co23; however, it is not clear from their article [17] whether or not the orthorhombic distortion was present at all in their sample. No orthorhombicity down to 100 K was observed recently in single crystals of HoBaCo$_4$O$_7$ [15]; however, the reason for such a suppression of the phase transition is not yet understood. When fitting our Mössbauer spectra of HoBaCo$_{3.9}$Fe$_{0.1}$O$_7$ at 300 K (figure 9) with two doublets, we observed the ratio of the areas of the doublets to be $4 : 1$, with 80% abundance of the narrower doublet. This is different from the ratio reported by Tsipis et al (3 : 2) [17]; however, the larger area reported by these authors for the minor doublet correlates with the smaller value of $\varepsilon_2$. Also, their value of $\varepsilon_1$ coincides with ours. This means that whole spectra at the ambient temperature are very similar, and the difference in fitting the spectra with two doublets can be caused by instrumental factors affecting the lineshape.

3.3.3. Comparison of HoBaCo$_4$O$_7$ to systems with charge/orbital ordering: dissimilarity of the EFG changes at $T_s$. The charge redistribution at $T_s$, seen not only via the change of the Co–O distances, but also via jumps of resistivity [3, 4], looks, after all, very different than a charge/orbital ordering. Much larger changes of quadrupole splitting across $T_s$ are usually expected when the charge ordering is driven by an orbital ordering. Huge jumps of $\varepsilon$ are typically associated with the orbital ordering. For example, in BiMn$_{0.95}$Fe$_{0.05}$O$_3$, the jump-like anomaly $\Delta \varepsilon = 0.4 \text{ mm s}^{-1}$ of quadrupolar splitting at $T_{00} = 414 \text{ K}$ was observed [18]. In the manganites of the family REBaMn$_{1.96}$Fe$_{0.04}$O$_6$, a fourfold increase of the quadrupole

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splitting was observed (at 300 K) in the charge and orbitally ordered compounds (RE = Y, Gd, Sm) compared to unordered ones (RE=La, Na, Pr) [19]–[21]. The orbital ordering coupled with charge ordering is therefore unlikely to drive the structural phase transition at $T_s$.

3.3.4. Analysis of the average EFG changes at $T_s$ within the displacive transition scenario. The narrow distribution of EFG over different Co sites is in agreement with very similar constitutions of their first coordination spheres. Three of four oxygens entering the 1st coordination sphere of each Co ion are O2 and O3. They account for 6/7 of the total oxygen content in HoBaCo$_4$O$_7$. The remaining 14.3% oxygen sites (O1-sites) are coordinated by four
With respect to the covalent Co–O bonding, a bridge-like (O2 and O3) and a tetrahedral (O1) oxygen are distinguished by fractional $p$-character of the bonds. The latter oxygen ion shows more ionic bonding and longer Co–O bonds. In terms of the point charge model, the negative charges located along each bond direction differ when the occupation number $n$ (generally fractional) of the $sp^n$-hybrids changes [22].

Thus, all Co ions are containing in their first coordination sphere three bridge-like oxygens and one tetrahedral oxygen. Two types of ligands for each Co presents the plausible argument to explain the rather narrow lines of the symmetric doublet observed in the Mössbauer spectra. In spite of the occurrence of four different sites for Co in the low-temperature phase, the spectrum shown in figure 9 evidences the narrow distribution of EFG over these sites. If we attribute the origin of EFG to a strong difference between the bridge-like and tetrahedral oxygen ligation, then the EFG can be explained in terms of the point charge model for the first coordination sphere. Then, due to the symmetry in the high-temperature phase, the EFG on each of the Co sites should be orientated along the longest Co–O1 bonds for both Co1 and Co2 sites.

The tetrahedra are nonideal rigid bodies; therefore, in the low-temperature phase, each of three tetrahedra in the Kagomé layer is distorted in its own way. However, we observe a change of $\epsilon$ within only 3%. This is an important observation, which would let us estimate whether or not the partial contribution of each ligand to EFG depends on the bond angles. Generally, upon variation of bond angles, the partial contribution to EFG may change because the fractional $p$-character of the bonds changes [22]. However, families of compounds exist in which the assumption of angle-independent partial contributions is a good approximation. Such families include, for example, brownmillerites and high-$T_c$ superconductors with ‘1212’ structure [23].

The high-$T_c$ cuprates, so different at first sight from brownmillerites, show very similar ligation for iron located at midway between the cuprate planes [23–25].

The quadrupole splitting is related to the EFG tensor main component $V_{zz}$ and EFG asymmetry $\eta = (V_{xx} - V_{yy})/V_{zz}$ via [25]:

$$\varepsilon = \frac{eQcV_{zz}}{2E_\gamma} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}. \quad (4)$$

Here $E_\gamma = 14.4125$ keV is the transition energy, and $Q$ is the quadrupole moment of the excited state of the $^{57}$Fe nuclei. From the EFG $V_{zz}$ in units of V m$^{-2}$ the quadrupole splitting in mm s$^{-1}$ can be obtained using the factor $\frac{1}{2}eQcE_\gamma^{-1} = 0.1664 \times 10^{-21}$ mm s$^{-1}$ V$^{-1}$ m$^2$ for the $Q$ value of 0.16 barn. Equation (5) shows that the changes in $\varepsilon$ signify either variation of $V_{zz}$ or variation of $\eta$ or both.

The behavior of $\eta$ is well predictable in the vicinity of a second-order phase transition. Displacive phase transitions are usually close to the continuous phase transitions, which, despite being described rigorously with renormalization group theory as first-order-like, in practice exhibit the size of first-order discontinuities so small as to be virtually unobservable [10]. Through the continuous phase transitions an empiric rule was established [11], which states that all three components of the EFG tensor depend linearly on a single control parameter. In other words, the changes of the principal component and asymmetry of the EFG tensor are correlated and both $V_{zz}$ and $\eta$ vary continuously through such a transition. Symmetry breaking obviously underlies this rule in vicinity of axiality ($\eta = 0$) or antiaxiality ($\eta = 1$).

The nontrivial correlation between $V_{zz}$ and $\eta$ is illustrated by the linear trajectories of the system in the so-called Czjzek plot, in which $-2V_{xx}$ is plotted versus $|V_{zz}|(\sqrt{3} + \eta/\sqrt{3})$ [11, 22]. These axes are chosen to make use of the intrinsic properties of the EFG tensor, which
Figure 11. (a) Czjzek plot of \( Y = V_{zz}(1 - \eta) = -2V_{xx} \) versus \( X = |V_{zz}|(\sqrt{3} + \eta/\sqrt{3}) = 2/\sqrt{3} \cdot |2V_{zz} + V_{xx}| \) with the EFG tensor components ordered according to \(|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|\). Lines originating from the origin are \( \eta = \) const. lines. The angles of inclination of the straight-line trajectories with respect to the abscissa axis are indicated. The arrows show the direction of increasing temperature. (b) Corresponding dependences of the EFG asymmetry \( \eta(T) \). The frames mark the \( \eta(T) \) curves for two trajectories whose EFG components are shown in detail in figure 12.

is symmetric and traceless. Therefore, in the condition of antiaxiality (at the horizontal axis in the Czjzek plot, figure 11(a)), where \( V_{zz} \) changes its sign by definition, the system passes the line \( \eta = 1 \) without refraction. On the other hand, at \( \eta = 0 \) the system reflects from the borders of the Czjzek plot with billiard kinematics. These properties are always satisfied when each component
of the EFG tensor depends linearly on a single control parameter \( p \) \cite{11}. This parameter is in turn a function of temperature \( p = F(T) \).

In figure 11(b), we plotted \( \eta \) versus \( T \) assuming several linear paths of the system in the Czjzek plot shown in figure 11(a). First of all, the path at the angle of \( \pi / 2 \) to the horizontal axis crosses the line \( \eta = 1 \) at the same temperature where \( \varepsilon(T) \) shows the minimum in figure 10. Therefore, the \( \eta(T) \) curve culminates at \( T = 70 \text{°C} \) in figure 11(b). Also, the trajectory, which starts at the angle of \( 2\pi / 3 \) near \( \eta = 0.4 \), goes to the upper border of the Czjzek plot, reflects from the \( \eta = 0 \) line backwards to the angle of \( -\pi / 3 \) and, returning back to \( \eta = 0.4 \), produces the curve \( \eta(T) \) with the minimum at \( T = 70 \text{°C} \). The path tilted to the midway angle with the directions towards \(( -5\pi / 12) \) and \(( 7\pi / 12) \) produces two \( \eta(T) \) curves with no extremum, but with a sigmoidal shape having the inflection again at \( T = 70 \text{°C} \). These two curves correspond to two opposite directions of increasing temperature along the same line indicated by arrows in the Czjzek plot (figure 11(a)).

Next, we investigate the trajectory tilted to the angles intermediate between \( 7\pi / 12 \) and \( 2\pi / 3 \). As in the case of \( 2\pi / 3 \), such a trajectory is reflected from the border of the Czjzek plot, but now not at the right angle. The path starting at the angle of \( 17\pi / 24 \) reflects to the angle of \( -3\pi / 8 \). Moving in the opposite direction along the same trajectory, we start from the short segment at the angle of \( 5\pi / 8 \) and reflect to \( -7\pi / 24 \). In both these cases, the reflection point does not coincide with the minimum of the \( \varepsilon(T) \) curve in figure 10. Because our experimental data for \( \varepsilon(T) \) are more or less symmetric relative to the minimum at \( T = 70 \text{°C} \), two possible trajectories for these angles generate two curves for \( \eta(T) \). One of them shows a minimum at \( T = 82 \text{°C} \) and another shows a minimum at \( T = 60 \text{°C} \).

In the same way, two trajectories in the Czjzek plot and two \( \eta(T) \) curves can be generated for the angles of \( -11\pi / 24 \) and \( 13\pi / 24 \) along the line intermediate between \( 7\pi / 12 \) and \( \pi / 2 \). These two paths cross the horizontal axis (\( \eta = 1 \) line) at different temperatures. Again the generated \( \eta(T) \) curves culminate at \( T = 82 \text{°C} \) and \( 60 \text{°C} \).

Since we know now both values of \( \eta(T) \) and \( |V_{zz}(T)| \) along each path in the Czjzek plot, we can derive each component of the EFG tensor. In the displacive limit, the behavior of \( \eta(T) \) in the vicinity of \( T_s \) is expected to follow closely the behavior of order parameter around the point where symmetry breaks \cite{11}. Two of the obtained \( \eta(T) \) curves culminate indeed at \( T_s = 82 \text{°C} \). Therefore, if we are indeed not far from the displacive limit, the EFG components \( V_{zz}, V_{yy} \) and \( V_{xx} \) should behave as shown in figure 12. In the first case (\( 5\pi / 8 \) to \( -7\pi / 24 \)), the EFG is nearly axial above \( T_s = 82 \text{°C} \), but quickly approaches antiaxiality as the hexagonal symmetry breaks down. The nonprincipal EFG components exchange their direction at \( T_s \). The second case (\( 13\pi / 24 \)) is opposite. In the second case, the principal EFG component switches its direction at \( T_s \). The plot in figure 12(a) corresponds to the appearance of the additional source of EFG below \( T_s \), which induces the second large EFG component. In contrast, the plot in figure 12(b) corresponds to the case when two large components of EFG exist above \( T_s \) and one of them is extinguished at the expense of the displacements showing up with the breakdown of symmetry.

Only the first case fits the high-temperature axially, which should correspond to our classification of the oxygen ligands as bridge-like and tetrahedral ones. In this case, the \( z \)-axis of the EFG in its internal coordinate system must be directed from each Co ion towards ionic tetrahedral oxygen O1 (in the radial direction of figure 13). In this picture, the small asymmetry of EFG above \( T_s \) arises from the structural difference between bridge-like oxygens O2 and O3. Because of non-ideal rigidity of tetrahedra below \( T_s \), the displacements of the O3 atoms are larger than the displacements of the O2 atoms. The change in the bond angles and the associated

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Figure 12. Variation of the EFG tensor components for two straight-line billiard trajectories in the Czjzek plot with the direction of increasing temperature inclined at the angle to the abscissa axis of $5\pi/8$ and reflected to $-7\pi/24$ (a) and $13\pi/24$ (b). Corresponding dependences $\eta(T)$ are marked by frames in figure 11(b).

change in the fractional $p$-character of these oxygen bonds result in the additional component of EFG, which becomes comparable in magnitude with the main EFG component.

Thus, although changes in $\varepsilon(T_s \pm \Delta T)$ were observed within only 3% we showed that the non-principal EFG components ($V_{xx}$ and $V_{yy}$) vary much more dramatically in the vicinity of $T_s = 355$ K in agreement with the local structure changes at the symmetry-breaking transition. Although the variations of each of three individual EFG components $V_{xx}$, $V_{yy}$ and $V_{zz}$ are smooth similarly to the temperature dependences of the lattice parameters $a$ and $b/\sqrt{3}$, we have demonstrated the nonmonotonic behavior of the combination $\eta(T) = (V_{xx} - V_{yy})/V_{zz}$, which experiences a dip-like (or cusp-like) anomaly at $T_s$. In the vicinity of $T_s$ the temperature dependence of the EFG asymmetry $\eta(T)$ is that of the order parameter as expected for a displacive phase transition.
4. Discussion

4.1. Changes in geometry of cationic coordination polyhedra: collapse of the $\text{BaO}_{12}$ anticubooctahedron by rotation of the $\text{CoO}_4$ tetrahedra

Huq et al [8] suggested the origin of the transition in YbBaCo$_4$O$_7$ to be a ‘response to a markedly underbonded Ba$^{2+}$ site in the high-temperature phase’. The ion Ba$^{2+}$ occupies an anticubooctahedral site. In an ideal anticubooctahedral coordination, there are 12 equidistant ligands. The geometry of the anticubooctahedron close to the ideal one was found in several studies of single-crystalline samples of REBaCo$_4$O$_7$ for RE = Ho [15], Lu [26]; however, it was severely distorted in other structural studies on single-[7] and poly- [8, 27] crystalline samples. The Ba–O distances of 3.14 ± 0.01 Å reported for the nearly ideal anticubooctahedron by Juarez–Arellano et al [15] in HoBaCo$_3$O$_7$ and Kozeeva et al [26] in LuBaCo$_3$O$_7$ seem to be too large for ordinary bondlengths of Ba$^{2+}$. No phase transition was reported for such samples. In other studies, the distortion of the anticubooctahedron was reported to shorten the shortest Ba–O bondlength down to 3.08 Å in YBaCo$_3$O$_7$ [7], 3.02 Å in HoBaCo$_3$O$_7$ [27] and 2.8 Å in YbBaCo$_3$O$_7$ [8]. The average Ba–O distances of 3.14 ± 0.02 are nearly independent of RE; however, the distortions in a much broader range were reported depending on the symmetry.

In each of the structure models, $P6_3mc$, $P31c$, $Cmc2_1$ and $Pbn_2_1$, the distortion of the anticubooctahedron makes a number of Ba bondlengths increase, and the same number of Ba bondlengths to decrease. The average Ba–O distance remains unchanged. Namely, within the $P6_3mc$ model, 6 of 12 oxygens remain at the ideal distances, three of them are allowed to move inwards and three others outwards of the ideal anticubooctahedron. For the $Cmc2_1$ model, such a ratio changes from 3 : 6 : 3 to 5 : 2 : 5. The lower symmetries $P31c$ and $Pbn_2_1$ allow the distortion ratio 6 : 0 : 6; however, in YbBaCo$_3$O$_7$, Huq et al [8] obtained within the $P31c$ model the anticubooctahedron distortion scheme 3 : 6 : 3 similar to that of the $P6_3mc$ model. This means the very small changes of bondlengths of six oxygens compared to the ideal anticubooctahedron. Therefore, the authors argued that the change of the distortion scheme of the anticubooctahedron from ‘3 : 6 : 3’-like above $T_s$ to 6 : 0 : 6 below $T_s$ is at the origin of the phase transition. This conclusion is not contrary to our viewpoint, especially because we fitted successively the high-temperature phase only with the $P6_3mc$ model, which is intrinsically distorted according to the same 3 : 6 : 3 scheme. Although both the $P6_3mc$ and $P31c$ models result in similar $R$-factors for the high-temperature phase, only the $P6_3mc$ model gave us plausible interatomic distances. Indeed, when trying to fit the high-temperature phase with the $P31c$ model, we obtained the distortion of the anticubooctahedron much larger than that reported by Huq et al [8]. In addition, the unrealistic Co–O distances of the order of 1.7 Å resulted, which obliged us to reject the $P31c$ model.

Thus the driving force of the transition to lower symmetry is likely to arise from too loose bonding of Ba$^{2+}$ in the symmetric anticubooctahedron. While the Ba$^{2+}$ coordination polyhedron tends to collapse with lowering temperature, we do not observe that the coordination polyhedra of the Co ions change so dramatically. Displacive phase transitions in the tetrahedral networks are frequently driven by a soft optic phonon, which can propagate without distortions of tetrahedra. Such modes were called rigid-unit modes (RUMs) [28].

4.2. Frame of reference for librations and rotations: the ‘hinges’ in structure

The coordination polyhedron of Ba$^{2+}$ is formed by O2 and O3 atoms. Each of these oxygens enters the first coordination sphere of two Co, two Ba$^{2+}$ and one Ho$^{3+}$. On the other hand, the O1
atom enters the first coordination sphere of four Co ions. Therefore, the deformation of the Ba\(^{2+}\) coordination corresponds to the motion of O2 and O3 atoms, which would also be represented in terms of the Kagomé network as the motion of the O2 and O3 tetrahedral vertices around the O1 vertex. This is because each Co in the Kagomé layer (Co2 site) is coordinated by one O1, one O3 and two O2 atoms.

Since in the covalent bonding is stronger within the framework of the CoO\(_4\) tetrahedra compared to the ionic bonding on the exterior of the framework, the distortion of the tetrahedra will cost more energy. The associated with such a distortion phonon modes would lie rather high on the frequency scale. In contrast, the RUMs that do not involve any significant stretching of the Co–O bonds will have low frequencies. One of the low-energy RUMs appears to be strongly temperature dependent to become a soft mode driving the phase transition. This mode permits the intertetrahedral motions associated with the bending of the Co–O–Co links, where the central O atom can be viewed as a ‘hinge’. The rotations of tetrahedra around the ‘hinges’ are hindered either by the size of the collapsed cavity around Ba\(^{2+}\) or by repulsion between oxygens getting too close to each other. Such hindered rotations named librations are commonly observed in tetrahedral networks [29]. In figure 13, the O ‘hinge’ can be identified at the O1 atom (exactly at the center of the top panel in figure 7).

From figure 7, it is evident that our low-temperature phase is quite similar to that reported for YbBaCo\(_4\)O\(_7\) [8]. It is also clear that the low-temperature phase can be obtained from the high-temperature one via quenching the positions of the O3 atoms at the endpoints of a counterclockwise rotation. Since the O3 site splits into three below \(T_s\), the rotation angles are different (in the range between 5° and 10°) for O31, O32 and O33. The rotation axis [001] is the same for O31, O32 and O33; therefore, these oxygens keep their planar arrangement as in the high-temperature phase (see the central plane at the bottom of T-layer in figure 1).

According to the RUMs concept, the axial rotation of the tetrahedral vertices located on top (in terms of figure 1) of the Kagomé layers cannot occur without \(z\)-displacements of the O2 atoms at the bottom of these Kagomé layers. This is because only 25% of the oxygens at the bottom of Kagomé layers are located on the rotation axes. These O1 atoms constitute the rotation ‘hinges’. The other 75% oxygen sites in this plane are the O2 sites, which split into O21, O22 and O23 in the low-temperature phase. Owing to the rotation of the tetrahedral

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**Figure 13.** The star-like fragment of the Kagomé layer showing the surroundings of the O1 ‘hinge’ below \(T_s\).
‘rigid units’, the O21 and O22 atoms get out of the plane, in which they were in the high-
temperature phase.

4.3. Origin of the orthorhombicity

The shift of the O21 site along the $z$-axis is as large as 0.52 Å. This is consistent with the largest 
rotation angle ($\approx 10^\circ$) for the O31 atom, which belongs to the tetrahedra of Co21 (in figure 7 
two of these tetrahedra form a vertical ‘sandglass’ figure extended along the $b$-axis around the 
central O1 atom). Smaller rotation angles are shown in figure 7 for the O32 and O33 atoms, 
which belong to the tetrahedra of Co22 and Co23, respectively. This is in agreement with a 
smaller out-of-plane $z$-shift of the O22 atoms (0.14 Å), which belong to both Co22 and Co23 
tetrahedra. The third site O23 remains at the same $z$-level as in the high-temperature phase. This 
site belongs to Co21 and Co23 tetrahedra.

Thus, the tetrahedra faces, which were parallel in the high-temperature phase, become 
slightly tilted relative to the horizontal plane. The measure of tilts for the bottom faces of Co21 
and Co23 tetrahedra are the $z$-shifts of the corresponding vertices, i.e. 0.52 and 0.14 Å, for 
Co21 and Co23 tetrahedra, respectively. The degree of tilt for the Co22 tetrahedra, which is 
formed by the O21 and O22 vertices, is measured by the difference of their $z$-shifts, that is, 
0.52–0.14 = 0.38 Å. This relationship directly follows from the symmetry $Pbn2_1$. Because of 
such a relationship between the values of $z$-shifts for O21, O22 and O23 atoms, the spread 
between the tilts of three tetrahedra surrounding the O1-hinge becomes unavoidable. Quite a 
similar spread was obtained by Huq et al [8]. If the tetrahedra are indeed behaving as rigid 
units, the related spread would in turn appear in the angles of rotation of the three O3 atoms 
around the O1–$z$ axis. Comparing the results of our refinement with the data of [8], we show in 
figure 7 that the spread is quite similar for HoBaCo$_4$O$_7$ and YbBaCo$_4$O$_7$.

In the high-temperature phase, where all three O3 atoms around the O1–$z$ axis are 
equivalent, they librate with equally large amplitudes as shown in the upper panel of figure 7. 
The thermal displacements of O3 atoms have no component along $z$; however, the $z$-component 
is the main component for O2 atoms (see the footnote of table 3). However, because the rigidity 
of tetrahedra put the constraint on the $z$-shifts of three O2 atoms, the rotations cannot be 
condensed below $T_s$ within the high-symmetry model $P6_3mc$, in which all of the O2 sites 
are equivalent. Therefore, the rigid-body libration of tetrahedra lowers the symmetry, so that 
the orthorhombicity directly follows from combining the RUM condensation with translation 
symmetry.

4.4. Content of the bridge-like oxygen ions (86%) in HoBaCo$_4$O$_7$: far from spinel, close to 
soft-mode-rich perovskites

In tetrahedral networks, various constraints on possible models of deformation of these networks 
were described previously by Dove et al [30]. The structure becomes highly susceptible to 
libration-like motions when the proportion of ‘bridge-like’ two-coordinated anions is large. For 
example, in the red mercury HgI$_2$, where all the anions are bridge-like, the coupled librations of 
HgI$_4$ tetrahedra are unconstrained and the thermal displacements of anions are strongly 
anisotropic [31]. This is not the case for the build-up from tetrahedra and octahedra structure 
of spinel M$_3$O$_4$, in which all the oxygens are four-coordinated. A detailed comparison of the 
structure of REBaCo$_4$O$_7$ with spinels, hexaferrites and perovskites with YBaFe$_3$O$_7$ ferrite was
recently made by Caignaert et al [32]. In the close-packed systems, the fraction of bridge-like oxygen increases with increasing the fraction of large-size cations. Maximum possible content of large-size cations entering the close packing is reached in perovskites where like in the red mercury all the oxygens are bridge-like.

4.5. Displacive transition scenario for increasing $T_s$ with an increase in the ionic size of the rare-earth site

Phase transitions known for the tetrahedral and octahedral networks are classified into displacive transitions and transitions of order–disorder type. In a simple model of double-well potential [10], the type of transition is determined by the relationship between the energy of harmonic forces among neighboring atoms ($\sim k_B T_s$) and the height of the barrier $V_0$ separating two minima of the potential well. The degree of displaciveness for a transition is given by the parameter $s^{-1} = k_B T_s / V_0$. We are in the displacive limit when $s^{-1} \gg 1$ and in the order–disorder limit when $s \gg 1$. Interestingly, an intermediate type of transition ($s \simeq 1$) was attributed to freezing the librations of large amplitude, such as librations of CO$_3$ groups to an angle of $\sim 30^\circ$ in calcite [10].

In the displacive limit, there exists a well-established relationship between the transition temperature and the angle of rotation of tetrahedra at 0 K:

$$k_B T_s = K \varphi_0^2.$$  

Markina et al [2] and Juarez-Arellano et al [15] have reported a nearly linear relationship between the value of $T_s$ in REBaCo$_4$O$_7$ and the size of ionic radii of RE. The temperature $T_s$ increases by two times when the size of RE increases by 4%. The radii of Yb and Ho differ by 3%. However, in figure 7, we observe that the values of $\varphi_0$ are very similar for RE = Yb and Ho. The force constant $K$ in equation (4) is the stiffness of the rigid-body unit. Therefore, if we are in the displacive limit, where equation (1) is valid, the linear relationship between $T_s$ and $K$ may signify the increase in strength of the Co–O bonds with an increase in the ionic radius of RE. This phenomenon can be regarded as the manifestation of the inductive effect [33] in the Kagomé network: Co–O bonding is reinforced at the expense of RE–O bonding. Indeed, all the O2 and O3 sites (85.7% of all oxygen sites) are coordinated by two Co, two Ba and one RE.

The inductive effect [33] related to decreased covalence of RE–O bonding with increasing the size of RE, would concern these O2 and O3 sites.

5. Concluding remarks and notes added

The hexagonal network structure of HoBaCo$_4$O$_7$ made up of star-like clusters of tetrahedra Co$_4$O$_{13}$ exhibits strong covalent bonding within the Co–O network and loosened ionic bonding for the Ba$^{2+}$ and Ho$^{3+}$ ions located within large cavities, anticubooctahedral and octahedral, respectively. In the Co–O network, the vibrational excitations transverse to the Co–Co directions have lower excitation energies than the longitudinal modes. The lower-energy transverse excitation must dominate the thermal motion in the temperature region of the phase transition. Therefore, the large transverse thermal displacements of O2 and O3 oxygen sites refined from our synchrotron data above $T_s$ are considered as a physically valuable observation. These sites are bridge-like, i.e. similar to the oxygen sites in perovskites, but are dissimilar to the oxygen sites in spinels. The amplitudes of transverse vibrations in such sites may reach so large
values typically when the whole coordination polyhedra librate as rigid units. Although in a recent work \[34\] the arguments were presented based on the Maxwell counting scheme for the evaluation of the stiffness of frames \[35\] that the framework of tetrahedra in these structures is overconstrained, the Maxwell relationship between the number of degrees of freedom and the number of constraints in HoBaCo$_4$O$_7$ is similar to that in perovskites. However, the structure of a perovskite is very susceptible to soft modes and rich by RUMs. The rectangularity of the perovskite structure allowing the occurrence of parallel bonds lifts over the extra constraints, making it possible for the RUMs to exist in the long range. On the other hand, we have shown above that the displacements that take place in the low-temperature phase are incompatible with hexagonal symmetry; therefore, they cannot be represented as frozen phonons of the high-temperature phase if these phonons are regarded as long-range plane waves. However, the bending flexibility provided by the Co–O–Co linkages via bridge-like oxygens allows for the low-energy excitations to occur on the short range and the medium range. The propagation of such quasilocal RUMs is not straight plane-wave-like, but must exhibit some features of diffusive motion. Clearly, a minor modicum of the bonds must be ‘partly broken’ or dynamically loosened to allow such a propagation. There are at least two theoretical models that elucidate these quasi-local modes ubiquitous in glasses but observed also in some crystalline systems. Rykov et al \[24\] have reviewed both of them: the so-called broken ladder model and the soft potential model. Examples of appearance of the quasi local low-energy excitations in crystalline systems \[24\] suggest that they are most common for systems containing the chains of tetrahedra. In oxygen-deficient perovskites, the event of ordering the oxygen vacancies in rows to form the chains of tetrahedra results in quasi local low-energy excitations. In many tetrahedral networks, the excess of low-energy excitations over the acoustic ones appears in the region of the Boson peak (below 8–10 meV) as a surplus of the DOS over the DOS predicted by the Debye model \[24\]. In the Kagomé layers of HoBaCo$_4$O$_7$, the star-like clusters of tetrahedra are arranged in such a way as to form three systems of chains running at the angle of 60° with respect to each other and interlaced at the O1-hinges. Despite the general rigidity of the triangular frames the string-like nature of the system manifests itself in the large transverse thermal displacements of the non-cross-linked bridge-like oxygens that may arise merely from the ‘quasi-rigid-unit’ floppy modes.

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