Focus Issue Paper

Structure and cation distribution in perovskites with small cations at the A site: the case of ScCoO₃

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Abstract
We synthesize ScCoO₃ perovskite and its solid solutions, ScCo₁₋ₓMₓO₃ and ScCo₁₋ₓCrₓO₃, under high pressure (6 GPa) and high temperature (1570 K) conditions. We find noticeable shifts from the stoichiometric compositions, expressed as (Sc₁₋ₓMₓ)MO₃ with x = 0.05–0.11 and M = Co, (Co, Fe) and (Co, Cr). The crystal structure of (Sc₀.₉₅Co₀.₀₅)CoO₃ is refined using synchrotron x-ray powder diffraction data: space group Pnma (No. 62), Z = 4 and lattice parameters a = 5.26766(1) Å, b = 7.14027(2) Å and c = 4.92231(1) Å. (Sc₀.₉₅Co₀.₀₅)CoO₃ crystallizes in the GdFeO₃-type structure similar to other members of the perovskite cobaltite family, ACoO₃ (A³⁺ = Y and Pr-Lu). There is evidence that (Sc₀.₉₅Co₀.₀₅)CoO₃ has non-magnetic low-spin Co³⁺ ions at the B site and paramagnetic high-spin Co³⁺ ions at the A site. In the iron-doped samples (Sc₁₋ₓMₓ)MO₃ with M = (Co, Fe), Fe³⁺ ions have a strong preference to occupy the A site of such perovskites at small doping levels.

Keywords: perovskites, cobaltites, high-pressure, low-spin Co³⁺ ions

1. Introduction

ABO₃ perovskite-type compounds, where A³⁺ = Y and La-Lu and B³⁺ = V, Cr, Mn, Fe, Co, Ni and Ni₀.₅Mn₀.₅, and their solid solutions have been attracting a lot of attention for decades from the viewpoints of fundamental physics and practical applications [1–3]. For example, some ACrO₃ compounds exhibit spin-reorientation transitions [4], and doped ACrO₃ are good oxygen-ion conductors and show sensitivity toward methanol, ethanol, some gases and humidity [5]. ACoO₃ compounds have been investigated a lot because of spin-state transitions in Co³⁺ ions and metal-insulator transitions [6]. ACoO₃ also exhibit thermoelectric
and B cations decreases the probability of the A/B inter-site mixing is increased in such perovskites. Noticeable cation mixing or, more precisely, shifts in the composition were found in \((\text{In}^{3+}_{1-x} \text{Mn}^{2+}_x)\text{Mn}_3\text{O}_4\) \((1/9 \leq y \leq 1/3)\) [15] and \((\text{Sc}^{3+}_{0.94}\text{Mn}^{2+}_{0.06})\text{Mn}_{0.68}\text{Ni}_{0.32}\text{O}_3\) [16]; in such perovskites, small divalent transition metals are located at the A site.

In this work, we investigated ScCoO\(_3\) perovskite and its solid solutions ScCo\(_{1-x}\)Fe\(_x\)O\(_3\) and ScCo\(_{1-x}\)Cr\(_x\)O\(_3\). We found noticeable shifts in the composition of such perovskites from ScCoO\(_3\) to \((\text{Sc}_{1-x}\text{Co}_x)\text{Co}_3\text{O}_4\) and the appearance of significant amounts of small trivalent cations (Co\(^{3+}\) and Fe\(^{3+}\)) at the A site. To the best of our knowledge, the presence of Fe\(^{3+}\) at the A site was detected for the first time in ABO\(_3\) perovskites.

2. Experimental details

Samples were prepared from stoichiometric mixtures of Sc\(_2\)O\(_3\) (99.9%), Co\(_3\)O\(_4\) (99.9%), Cr\(_2\)O\(_3\) (99.9%), Fe\(_2\)O\(_3\) (99.999%) and KClO\(_4\) (as the source of oxygen). The mixtures were prepared in a glove box, placed in Au capsules (in the amount of about 0.5 g for each sample) and treated at 6 GPa in a belt-type high-pressure apparatus at 1570 K for 2 h (heating rate to the desired temperature was 10 min). After the heat treatment, the samples were quenched to room temperature (RT), and the pressure was slowly released. The samples were washed in water to remove KCl obtained after the decomposition of KClO\(_4\).

X-ray powder diffraction (XRPD) data were collected at RT on a RIGAKU Ultima III diffractometer using CuK\(_\alpha\) radiation (2\(\theta\) range of 10–100\(^\circ\), a step width of 0.02\(^\circ\), and a counting time of 2s/step). Synchrotron XRPD data were measured at 293 K on a large Debye-Scherrer camera at the BL15XU beam line of SPring-8 [17]. The intensity data were collected between 1\(^\circ\) and 61.5\(^\circ\) at 0.003\(^\circ\) intervals in 2\(\theta\); the incident beam was monochromatized at \(\lambda = 0.65298\) Å. The samples were packed into Lindemann glass capillaries (inner diameter: 0.1 mm), which were rotated during measurements. Absorption coefficients were also measured, and Rietveld analysis was performed using the RIETAN-2000 program [18].

Electron probe microanalysis (EPMA) was performed using a JEOL JXA-8500F instrument. The surface of the pellets was polished on a fine alumina (0.3 \(\mu\)m) coated film before the EPMA measurements; and Sc\(_2\)O\(_3\) and Co\(_3\)O\(_4\) were used as standard samples for Sc and Co, respectively.

DC magnetic susceptibilities \((\chi = M/H)\) were measured using SQUID magnetometers (Quantum Design, MPMS-XL and 1T) between 2 and 400 K in different applied magnetic fields under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. FC measurements were performed on cooling (FC) from high temperatures to 2 K after the ZFC measurements. In all ZFC measurements, samples were rapidly (within 3–5 min) inserted into a magnetometer, which was kept at 10 K; then, temperature was set to 2 K, and finally a measurement magnetic field was applied. Isothermal magnetization measurements (M versus H) were performed.
between −70 and 70 kOe at 2 K and 300 K. Specific heat, \( C_p \), was recorded between 2 and 300 K on cooling at 0 and 90 K by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS). \(^{57}\)Fe Mössbauer spectra were recorded at 300 K using a conventional constant-acceleration spectrometer MS-1104Em in the transmission geometry. The radiation source \(^{57}\)Co(Rh) was kept at RT. All isomer shifts are referred to \( \alpha\)-Fe at 300 K. The experimental spectra were processed and analysed using methods of spectral simulations implemented in the SpectrRelax program \[19\]. Differential scanning calorimetry (DSC) curves of (Sc0.95Co0.05)CoO3 powder were recorded on a Mettler [19]. Differential scanning calorimetry (DSC) curves of (Sc0.95Co0.05)CoO3 powder were recorded on a Mettler

### Table 1. Structure parameters of (Sc0.95Co0.05)CoO3 and (Sc0.95M0.05)MO3 \((M = \text{Co}_{0.75}\text{Cr}_{0.25})\) at room temperature.

| Site | Wyckoff position | \( x \) | \( y \) | \( z \) |
|------|------------------|--------|--------|--------|
| Sc/Co | 4c | 0.07704(8) | 0.25 | 0.97603(12) | 0.333(9) |
| Co | 4b | 0 | 0 | 0.5 | 0.158(7) |
| O1 | 4c | 0.4468(3) | 0.25 | 0.1313(3) | 0.16(3) |
| O2 | 8d | 0.3101(2) | 0.0631(2) | 0.6830(2) | 0.22(2) |

The occupation factor of all sites is unity. Statistical distribution according to the compositions was assumed for the Sc/Co, Sc/M and M sites. Space group \( Pnma \) (No 62); \( Z = 4 \).

\[ \begin{align*}
(\text{Sc0.95Co0.05})\text{CoO3} & \approx \begin{pmatrix}
\text{Sc}^{3+} & \text{Co}^{3+} & \text{O}^{2-} \\
1 & 1 & 5
\end{pmatrix} \\
\text{Sc0.95Co0.05} & \approx \begin{pmatrix}
\text{Sc}^{3+} & \text{Co}^{3+} & \text{O}^{2-} \\
1 & 1 & 5
\end{pmatrix}
\end{align*} \]

The Mössbauer spectrum of (Sc0.95Co0.05)CoO3 crystallizes in the GdFeO3-type structure with space group \( Pnma \) similar to other members of the perovskite cobaltite family \( \text{ACoO3} \) \((\text{A}^{3+} = \text{Y} \text{ and Pr-Lu})\) (except for LaCoO3 \[6, 12\]). However, the unit cell volume of (Sc0.95Co0.05)CoO3 has just two cation positions: the first position is for the \( A \) cation, and the second for the \( B \) cation. The lattice parameters and unit cell volume of (Sc0.95Co0.05)CoO3 follow the general trends observed in the \( \text{ACoO3} \) \((\text{A}^{3+} = \text{Y} \text{ and Pr-Lu})\) family with low-spin \( \text{Co}^{3+} \) ions \[12\]. However, the unit cell volume of (Sc0.95Co0.05)CoO3 is smaller than that of ScAlO3 \((V = 185.915 \, \text{Å}^3)\) with the \( A^{1+} \) radius of 0.545 Å \[21\].

The Mössbauer spectrum of (Sc0.95M0.05)MO3 \((M = \text{Co}_{0.95}\text{Fe}_{0.05})\) at 300 K is shown on figure 2(a). It clearly consists of two doublets, Fe1 and Fe2, whose isomer shift \((\delta_{\text{Fe1}} < \delta_{\text{Fe2}})\) and quadrupole splitting \((\Delta_{\text{Fe1}} < \Delta_{\text{Fe2}})\) values indicate that the high-spin (HS) \( \text{Fe}^{3+} \) ions occupy two positions with different oxygen surrounding. The existence of these doublets could only originate from \( \text{Fe}^{3+} \) ions in positions corresponding to the \( A \) and \( B \) sublattices. The \( \delta_{\text{Fe1}} \approx 0.32(1) \, \text{mm s}^{-1} \) and \( \Delta_{\text{Fe1}} \approx 0.42(1) \, \text{mm s}^{-1} \) values for the first Fe1 doublet are in good agreement with the \( \delta = 0.31-0.33 \, \text{mm s}^{-1} \) and \( \Delta = 0.38-0.50 \, \text{mm s}^{-1} \) values for \( \text{Fe}^{3+} \) ions located in the \( B \) site of \( \text{RCO}_{0.98}\text{Fe}_{0.02}\text{O}_{3} \) \((\text{R} = \text{Y}, \text{Eu} \text{ and Lu})\) perovskites \[22\]. Taking into account that an increase in the average \((\text{Fe}-\text{O})\) distances leads generally to an increase in \( \delta \) values \[23\], the Fe2 doublet with the larger isomer shift of \( \delta_{\text{Fe2}} \approx 0.45(1) \, \text{mm s}^{-1} \) should correspond to \( \text{Fe}^{3+} \) ions located at the larger \( A \) site, and the larger quadrupole splitting
of $\Delta_{\text{Fe}2} = 1.26(1) \text{ mm s}^{-1}$ indicates that Fe$^{3+}$ ions have highly asymmetric coordination at the A site. It is expected that smaller 3d transition metals (Cr$^{3+}$, Fe$^{3+}$ and Co$^{3+}$) should be displaced off the position occupied by the larger Sc$^{3+}$ ions similar to the displacement of Mn$^{2+}$ ions found in Sr$_{0.98}$Mn$_{0.02}$TiO$_3$ [10]. Based on experimental values of the areas of the two doublets ($I_{\text{exp}}$ values in table 3), the distribution of $^{57}$Fe$^{3+}$ ions is not statistical (the statistical distribution would result in about 5% of $^{57}$Fe$^{3+}$ ions at the A site), but $^{57}$Fe$^{3+}$ ions preferably occupy the A site (about 30%).

To verify the correctness of the doublet assignment to the A and B positions, we calculated a lattice contribution ($V_{\text{lat}}$) to the electric field gradient (EFG) tensor at $^{57}$Fe at the A and B positions, using the experimental crystallographic data of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ (table 1). After diagonalization, the main EFG tensor components ($|V_{XX}| \geq |V_{YY}| \geq |V_{ZZ}|$) were used to estimate the theoretical quadrupole splitting $\Delta_{\text{theor}} = |eQV_{ZZ}/2(1 + \eta^2/3)|^{1/2}$, where $\eta \equiv (V_{XX} - V_{YY})/V_{ZZ}$ is the parameter of asymmetry of EFG. The best agreement between the theoretical ($\Delta_{\text{theor}} = 0.32 \text{ mm s}^{-1}$ and $\Delta_{\text{theor}} = 0.56 \text{ mm s}^{-1}$) and experimental values (table 3) of quadrupole splitting ($\Delta_{\text{exp}}$) was obtained for the oxygen dipole polarizability of $\alpha_O \approx 0.6 \text{ Å}^4$ (for nominal charges of $Z_{\text{Sc}} = -2$, $Z_{\text{Co}} = +3$ and $Z_{\text{O}} = +3$, and the quadrupole moment of $^{57}$Fe nuclei of $Q = 0.21 \text{ barns}$ [24]). The obtained high value of $\alpha_O$ agrees well with the data for other oxides [25]. The main factors, which can be responsible for the observed discrepancy between the $\Delta_{\text{theor}}$ and $\Delta_{\text{exp}}$ values, are the uncertainty in choosing the effective charges on the ions (Sc, Co and O) and the nucleus quadrupole moment $eQ$ for $^{57}$Fe nuclei [24]. However, our calculations qualitatively correctly predict the ratio of the $\Delta_i$ values ($\Delta_{B}^{\text{theor}}/\Delta_{A}^{\text{theor}} = 0.57$ and $\Delta_{\text{Fe}1}^{\text{exp}}/\Delta_{\text{Fe}2}^{\text{exp}} = 0.33$, see table 3) thus confirming that our model, which was used for the fitting and interpretation of the experimental spectrum, is reliable, and the Fe1 and Fe2 doublets are correctly assigned to the B and A positions, respectively, in the structure of (Sc$_{0.95}$M$_{0.05}$)MO$_3$ ($M = \text{Co}_{0.95}^{57}\text{Fe}_{0.05}$).
We observed no difference between the ZFC and FCC curves measured at low magnetic fields (e.g., 0.1 kOe) and high magnetic fields (e.g., 70 kOe) (Figure 3(a)). At high temperatures, almost no difference was found in magnetic susceptibilities measured at 0.1 and 70 kOe; however, at low temperatures, magnetic susceptibilities were suppressed by high magnetic fields in agreement with the isothermal $M$ versus $H$ curves (Figure 4(a)). ($\text{Sc}_{0.95}\text{Co}_{0.05}\text{CoO}_3$) exhibits paramagnetic behaviour (Figure 3(a)) with a relatively large effective magnetic moment of $\mu_{\text{eff}} = 1.749(6)\mu_B$/f.u. ($\mu_B$ is the Bohr magneton and f.u. is the formula unit) and the Curie–Weiss temperature of $\theta = -130(3)$ K. It is expected that Co$^{3+}$ ions at the B site should be in the non-magnetic low-spin (LS) state similar to other members of the A$^{3+}$CoO$_3$ (A$^{3+}$ = Y and Table 3. Hyperfine parameters of the $^{57}\text{Fe}$ Mössbauer spectra of ($\text{Sc}_{0.95}M_{0.05}$)MO$_3$ ($M = \text{Co}_{0.95}^{57}\text{Fe}_{0.05}$) and ($\text{Sc}_{0.89}M_{0.11}$)MO$_3$ ($M = \text{Co}_{0.6}\text{Fe}_{0.4}$) at 300 K.

| Sample                                      | Sites | $\delta$ (mm s$^{-1}$) | $\Delta$ (mm s$^{-1}$) | $W$ (mm s$^{-1}$) | $I$ (%) |
|---------------------------------------------|-------|------------------------|------------------------|------------------|--------|
| ($\text{Sc}_{0.95}M_{0.05}$)MO$_3$          | Fe1   | 0.32(1)$^a$            | 0.42(1)$^a$            | 0.31(2)          | 69(1)  |
| ($M = \text{Co}_{0.95}^{57}\text{Fe}_{0.05}$) | Fe2   | 0.45(2)                | 1.26(2)                | 0.34(1)          | 31(2)  |
| ($\text{Sc}_{0.89}M_{0.11}$)MO$_3$         | Fe1   | 0.33(2)$^a$            | 0.55(3)$^a$            | 0.25(2)          | 88(2)  |
| ($M = \text{Co}_{0.6}\text{Fe}_{0.4}$)     | Fe2   | 0.43(2)                | 1.30(2)                | 0.28(1)          | 12(2)  |

$^a$ These are the average $\langle \delta_{\text{Fe1}} \rangle$ and $\langle \Delta_{\text{Fe1}} \rangle$ values obtained from the distribution functions $p(\delta_{\text{Fe1}})$ and $p(\Delta_{\text{Fe1}})$.

$\delta$ is an isomer shift, $\Delta$ is quadrupole splitting, $W$ is linewidth, and $I$ is a relative intensity.

Figure 3. ZFC (filled symbols) and FCC (empty symbols) uncorrected magnetic susceptibility ($\chi$ = $M$/H) curves at 100 Oe and 70 kOe for (a) ($\text{Sc}_{0.95}\text{Co}_{0.05}\text{CoO}_3$) and (b) ($\text{Sc}_{0.95}M_{0.05}$)MO$_3$ ($M = \text{Co}_{0.95}^{57}\text{Fe}_{0.05}$). The right-hand axes give inverse FCC curves ($\chi$ versus $T$) at 70 kOe. Parameters ($\mu_{\text{eff}}$ and $\theta$) of the Curie–Weiss fits (bold lines) between 300 and 400 K are given. The thin lines show the same FCC $\chi$ versus $T$ curves at 70 kOe corrected for contributions from diamagnetic sample holders and core diamagnetism.

Figure 4. (a) Uncorrected $M$ versus $H$ curves of ($\text{Sc}_{0.95}\text{Co}_{0.05}\text{CoO}_3$) at 2 K and 300 K (symbols with the line). The line shows the Brillouin function with $g = 2$ and $S = 2$ at 2 K, multiplied by 0.028. (b) $M$ versus $H$ curves of ($\text{Sc}_{0.95}M_{0.05}$)MO$_3$ ($M = \text{Co}_{0.95}^{57}\text{Fe}_{0.05}$) at 2 K and 300 K (symbols with the line). The line shows the Brillouin function with $g = 2$ and $S = 5/2$ at 2 K, multiplied by 0.036. Broken lines show $M$ versus $H$ curves corrected for diamagnetic sample holders and core diamagnetism.
Pr-Lu) family [6, 26]; the temperature of the spin-state (LS-to-HS) transition increases sharply with decreasing the size of the A type cation [6]. Therefore, a large effective magnetic moment should originate from the high-spin Co$^{3+}$ ions located at the A site. The expected calculated effective magnetic moment is 1.124μB (for 0.0526Co$^{3+}$), which is close to the experimentally obtained value. Large effective magnetic moments and Curie–Weiss temperatures were also observed in LaCo$_{1-x}$M$_x$O$_3$ ($M$ = Rh and Ir) [27]; μ$_{\text{eff}}$ for the impurity-related magnetism is usually one order of magnitude smaller [28]. Magnetic properties of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ were very similar with those of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ (figure 3(b), with a slightly larger μ$_{\text{eff}}=2.050(4)$μB/μm. because of the presence of Fe$^{3+}$ ions (the expected μ$_{\text{eff}}$ is about 1.63μB). Note that the intrinsic magnetic moment of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ is quite small at high temperatures; therefore, diamagnetic contributions (from sample holders and core diamagnetism) have a significant influence on the μ$_{\text{eff}}$ and θ values (figure 3) making it difficult to discuss them.

The isothermal M versus H curves of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ and (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ ($M$ = Co$_{0.95}$Fe$_{0.05}$) showed no hysteresis and passed through the origin (figure 4); no saturation behaviour was also observed at 2 K, in contrast with the expected property for free ions, that is, the Brillouin function behaviour. The M versus H curve of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ was linear at 300 K up to 70 Koe. Deviations from the Brillouin function behaviour was observed in some doped LaCoO$_3$ samples [29]. Specific heat of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ is given on figure 5; between 9 and 31 K, the data follow the equation $C_p/T=\gamma+\beta T^2$ with $\gamma=7.86(8)$ mJmol$^{-1}$ K$^{-2}$ and $\beta_1=0.05452(17)$ mJmol$^{-1}$ K$^{-4}$ (the line in the inset of figure 5). Taking into account the fact that (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ is an insulator, the upturn of the $C_p/T$ values below 9 K and the apparent electronic contribution $\gamma$ could originate from Schottky-type contributions or single-ion excitations. The $\beta_1$ value of (Sc$_{0.95}$Co$_{0.05}$)CoO$_3$ was close to that of ScRhO$_3$ ($\beta_1=0.0589$ mJmol$^{-1}$ K$^{-4}$) [28].

The presence of Co$^{3+}$ ions in the LS and HS states is in qualitative agreement with the energy diagrams of Co$^{3+}$ in crystal fields with local symmetries of $O_h$ for the A position, in the first approximation (figure 6) [30]. In the case of the same average bond distances (Co-O), the crystal field splitting, $5/2-3\alpha_4$ (where $\alpha_4\sim 1/[\text{(Co-O)}]^{5/2}$ is a radial integral), of Co$^{3+}$ orbitals for the $O_h$ octahedral site is higher than the crystal field splitting for the $D_{4h}$ site (16/27α$^4$). Moreover, the average (Co-O) bond distances are longer in the A position in comparison with the B position (table 2), thus, further reducing the 16/27α$^4$ value and the crystal field splitting. In the case of the $O_h$ octahedral site, where the LS state of Co$^{3+}$ is experimentally realized, it gives $\alpha_4>6/5J_H$, where $J_H$ is the intraatomic Hund energy, $[E_{\text{LS}}-E_{\text{HS}}=(6\times(-2/3\alpha_4)+2\times(-3J_H))-(1\times(-2/3\alpha_4)+(-10J_H))]<0$. The $\alpha_4$ should be larger than $\alpha_2$ and with the same $J_H$ for Co$^{3+}$, the above conditions result in the HS state of Co$^{3+}$ at the $D_{4h}$ site. Note that the HS state of Co$^{3+}$ was experimentally found in BiCoO$_3$ [31], where Co$^{3+}$ ions are located in a square pyramidal coordination.

By the analogy with Sc$_{0.9}$CoO$_{2.85}$, we prepared solid solutions with the total composition of Sc$_{0.9}$Co$_{1-x}$Fe$_{0.25}$O$_{2.85}$ ($x=0.2, 0.4, 0.6$ and $0.8$). However, the samples with $x=0.2, 0.4$ and 0.6 contained Sc$_2$O$_3$ impurity (figure 7) suggesting...
that the chemical composition of the perovskite phases is further shifted. Sc$_{0.9}$Co$_{1-x}$Fe$_x$O$_{2.85}$ already contained a large amount of ScFeO$_3$ impurity with the corundum structure [32]. The lattice parameters of the solid solutions Sc$_{0.9}$Co$_{1-x}$Fe$_x$O$_{2.85}$ are shown on figure 8. Monotonic changes of the lattice parameters were found with a deviation for the two-phase sample with $x=0.8$; this fact suggests that the solid solution limit is near $x=0.7$.

Almost single-phase Sc$_{0.8}$Co$_{0.6}$Fe$_{0.4}$O$_{2.7}$ (≈(Sc$_{0.89}$M$_{0.11}$)MO$_3$ with $M=Co_{0.6}Fe_{0.4}$) was prepared whose Mössbauer spectrum at 300 K is shown on figure 2(b). The spectrum also consisted of two quadrupole doublets, Fe1 and Fe2, but in contrast to (Sc$_{0.95}$M$_{0.05}$)MO$_3$ ($M=Co_{0.95}Fe_{0.05}$), the most intense doublet Fe1 had broadened and asymmetrical components that could be caused by the existence of different configurations {$(6-m)Co^{3+}, mFe^{3+}$} in the local surrounding of the Fe$^{3+}$ ions within the B sublattice. We fitted the experimental spectrum as a superposition of a discrete doublet Fe2 and a distribution $p(\Delta_{Fe1})$ of the quadrupole splittings ($\Delta_{Fe1}$), assuming a linear relation between $\Delta_{Fe1}$ and $\delta_{Fe1}$ [33]. For comparison, a similar fitting analysis was carried out for (Sc$_{0.95}$M$_{0.05}$)MO$_3$ ($M=Co_{0.95}Fe_{0.05}$) (table 3); note that the Mössbauer parameters for this sample in two models (the first model is two discrete doublets, and the second one with a distribution for Fe1) were almost identical. The obtained $p(\Delta_{Fe1})$ distributions are shown in figure 2(c), and the best-fit hyperfine parameters (average ($\delta_{Fe1}$) and ($\Delta_{Fe1}$) values for the Fe1 subspectra) and relative intensities ($I_{Fe1}$) of the partial spectra are listed in table 3. A comparison of these data shows that changing the iron content in the samples does not significantly affect hyperfine parameters of the Fe1 and Fe2 doublets, while their relative intensities undergo some changes. According to the experimental intensity ratio of the partial spectra, $I_{Fe1}/I_{Fe2}$ (table 3), in the case of (Sc$_{0.95}$M$_{0.05}$)MO$_3$ ($M=Co_{0.95}Fe_{0.05}$), Fe$^{3+}$ ions were distributed almost statistically between the $A$ and $B$ sites (statistical distribution would give 10% of Fe$^{3+}$ at the $A$ site, and the experimental doublet area is 12(2)%). The resulting distribution $p(\Delta_{Fe1})$ for (Sc$_{0.95}$M$_{0.05}$)MO$_3$ ($M=Co_{0.95}Fe_{0.05}$) is narrow and has symmetrical profile, thus, indicating a uniform nearest surrounding of Fe$^{3+}$ ions.

The location of small Fe$^{3+}$ ions at the $A$ site of classical ABO$_3$ perovskites is quite unusual, especially their strong preference to occupy the $A$ site at small doping levels. To the best of our knowledge, (Sc$_{1-x}M_x$)MO$_3$ compounds are the first example of such behaviour. It should be noted that Fe$^{3+}$ ions were found by the Mössbauer spectroscopy at the $A'$ site of $A$-site ordered perovskites with the general composition of $AA'$$_2$BO$_3$, for example, in CaCu$_2$Fe$_2$O$_{12}$ [34] and CaMn$_2$Mn$_2$O$_{12}$ [35]. However, Fe$^{3+}$ ions substitute for Cu$^{2+}$ or Mn$^{3+}$ ions—other transition metals—in a special $A'$ position, whose coordination environment (square-coordinated $A'$ O$_4$) is quite different from a typical coordination of the $A$ site in perovskites (AO$_8$-AO$_{12}$).
We found that ‘ScCoO₃’-based perovskites are formed as non-stoichiometric (Sc₁₋ₓMₓ)O₃ with x = 0.05–0.11 and M = (Co, Fe) and (Co, Cr) under high pressure (6 GPa) and high temperature (1570 K) conditions. There is evidence that (Sc₀.₉₅Co₀.₀₅)O₃ has non-magnetic low-spin Co³⁺ ions at the B site and paramagnetic high-spin Co³⁺ ions at the A site. In the iron-doped samples (Sc₁₋ₓMₓ)CoO₃ with M = (Co, Fe), Fe³⁺ ions have strong preference to occupy the A site of such perovskites that is quite unusual for perovskites.

4. Conclusions

We also prepared solid solutions with the total composition of Sc₀.₉₅Co₀.₅Cr₀.₂₅O₃ (x = 0.25 and 0.5). The structural parameters of (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Sc₀.₇₅Co₀.₂₅) and (Co₀.₅Cr₀.₅) are given in tables 1 and 2; and the compositional dependence of the lattice parameters suggest that the solid solutions are formed in the whole compositional range. Inverse magnetic susceptibilities of (Sc₀.₉₅Co₀.₅Cr₀.₂₅) and (Sc₀.₅Cr₀.₅) are given on figure 9. The χ⁻¹ values were almost field-independent above 70 K for (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Sc₀.₇₅Cr₀.₂₅) and above 100 K for (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Co₀.₇₅Cr₀.₂₅) suggesting an impurity-free paramagnetic behaviour. The Curie–Weiss fits of the data corrected for diamagnetic contributions gave $\mu_{\text{eff}} = 2.47 \mu_B/f.u.$ and $\theta = -144$ K for (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Co₀.₇₅Cr₀.₂₅) with the expected $\mu_{\text{eff}} = 2.20 \mu_B/f.u.$ and $\mu_{\text{eff}} = 2.99 \mu_B/f.u.$ and $\theta = -107$ K for (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Co₀.₇₅Cr₀.₂₅) with the expected $\mu_{\text{eff}} = 2.91 \mu_B/f.u.$ The anisotropy at 100 Oe below 70 K in (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Co₀.₇₅Cr₀.₂₅) and below 100 K in (Sc₀.₉₅Co₀.₅Cr₀.₂₅)O₃ (M = Co₀.₇₅Cr₀.₂₅) could originate from the onset of short-range or long-range magnetic interactions.

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References

[1] Mitchell R H 2002 Perovskites: Modern and Ancient (Ontario: Almaz, Thunder Bay)
[2] Giaquinta D M and zur Lorey H C 1994 Chem. Mater. 6 365–72
[3] Izyumskaya N, Alivov Y and Morkoc H 2009 Crit. Rev. Solid State Mater. Sci. 34 89–179
[4] Preethi Meher K R S, Wahl A, Maignan A, Martin C and Lebedev O 2014 Phys. Rev. B 89 144401
[5] Sardar K, Lees M R, Kashtiban R J, Sloan J and Walton R I 2011 Chem. Mater. 23 48–56
[6] Takahata M, Yoshida T, Kawaji H, Atake T and Takayama-Muromachi E 2008 Phys. Rev. B 77 094402
[7] Baiker A, Marti P E, Keusch P, Fritsch E and Reller A 2009 J. Alloys Compd. 484 246–8
[8] Hashimoto H, Kusunose T and Sekino T 1994 J. Catal. 146 268–76
[9] Kolod nazhnyi T 2014 J. Eur. Ceram. Soc. 34 1741–53
[10] Levin I, Krayzman V, Woicik J C, Tkach A and Vilarinho P M 2010 Appl. Phys. Lett. 96 052904
[11] Choudhury D et al 2012 Phys. Rev. Lett. 108 127201
[12] Belik A A and Yi W 2014 J. Phys.: Condens. Matter 26 163201
[13] Markkula M, Arevalo-Lopez A M, Kusmartseva A, Rodgers J A, Ritter C, Wu H and Attfield J P 2011 Phys. Rev. B 84 094450
[14] Castillo-Martinez E, Bieringer M, Shafii S P, Cranswick L M D and Alario-Franco M A 2011 J. Am. Chem. Soc. 133 8552–63
[15] Belik A A, Matsushita Y, Tanaka M and Takayama-Muromachi E 2010 Angew. Chem. Int. Edn 49 7723–7
[16] Thomas C I, Suchomel M R, Duong G V, Fogg A M, Claridge J B and Rosseinsky M J 2014 Phil. Trans. R. Soc. A 372 20130012
[17] Tanaka M, Katsuya Y and Yamamoto A 2008 Rev. Sci. Instrum. 79 075106
[18] Tanaka M, Katsuya Y, Matsushita Y and Sakata O 2013 J. Ceram. Soc. Jpn. 121 287–90
[19] Izumi F and Ikeda T 2000 Mater. Sci. Forum 321–324 198–203
[20] Matsnev M E and Rusakov V S 2012 AIP Conf. Proc. 1489 178–85
